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THE EFFECT OF REACTOR PACKING ON THE  
PYROLYSIS OF HYDROCARBONS

by



T.N. HIGGINS

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled THE EFFECT OF REACTOR PACKING ON THE PYROLYSIS OF HYDROCARBONS submitted by T.N. Higgins in partial fulfilment of the requirements for the degree of Master of Science.



## ABSTRACT

Some parameters affecting the design and construction of vapor phase pyrolyzers are discussed. A reactor and furnace suitable for the vapour phase pyrolysis of hydrocarbons was constructed. Reaction parameters which affect the extent of pyrolysis and the pattern of pyrolysis are discussed. Experiments were performed to determine optimal reaction conditions for the reactor constructed. A steel reactor was constructed and the pyrolysis obtained in this reactor did not differ significantly from the pyrolysis obtained in a quartz reactor.

The optimal reaction conditions found in these experiments were then used to determine the effect of different reactor packings on the pyrolysis of hexane, 2,2-dimethylbutane, 2,3-dimethylbutane. It was found that the reactor packing used affects both the extent of pyrolysis and the pyrolysis pattern.



## DEDICATION

This thesis is dedicated to my parents without whose help, encouragement and example it would never have been written.



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## PRINCIPAL SYMBOLS

$D$	Diffusion coefficient
$F_m$	Uncorrected flow rate measured at the outlet system
$F_m^0$	$F_m$ corrected to 0°C, 760 mm of mercury, and for the vapor pressure of water
$F_o$	Flow rate at the entrance to the pyrolysis unit (0°C, 760 mm Hg)
$L$	Length of pyrolysis zone
$P$	Pressure
$P_p$	Pressure inside reactor
$P_w$	Vapor pressure of water
$r$	Radius of pyrolysis tube
$T$	Temperature
$T_p$	Pyrolysis temperature
$T_s$	Temperature of surroundings
$V_{\text{react}}$	Volume of heated zone of pyrolyzer
$\alpha$	Extent of reaction
$\tau$	Residence time



## CHAPTER I

### INTRODUCTION

#### 1.1 General Background

Since its introduction in 1952 gas liquid chromatography (g.l.c.) has found wide use as a separatory tool. Despite its wide use gas liquid chromatography suffers from several major disadvantages, one of which is the inability to identify the separated components, since most detectors used in gas liquid chromatography are non-specific.

In overcoming this problem of identification two types of approaches have been made.

The first approach involves the use of retention data to identify the separated components. For an homologous series it is possible to establish a relation between retention time and carbon number. Thus by knowing that the substance belongs to a certain series and its retention time it is possible to identify the substance as a particular member of the series (11). Another method involves the use of Kovats "retention indices" (16) which is based on retention time data. Both these methods suffer from the disadvantage of limited applicability. The first on the grounds that some prior knowledge of the sample is needed, the second on the grounds that widely different compounds have similar retention indices. Both are of limited value in the analysis of compounds above  $C_{10}$ .



The second approach has been the use of auxillary identification tools coupled to the outlet of the g.l.c. The combination of mass spectroscopy-gas chromatography is extensively used, less widely used is the combination of optical spectroscopy-gas chromatography. The latter method has only limited applicability since optical spectroscopy gives only limited structural information about certain classes of compounds, i.e., hydrocarbons. The mass spectroscopy-gas chromatographic system is expensive.

A simple, inexpensive system from which considerable structural information may be obtained is based on the thermal decomposition of the separated components with subsequent analysis of products. This technique known as pyrolysis gas chromatography (P.G.C.) has been applied to the analysis of a wide variety of materials. The main emphasis has been on the analysis of non volatile materials, i.e., substances such as polymers (3) and high melting solids (12) have been analyzed by this method. Lately the analysis of volatile compounds has been investigated. It would be wrong to suggest that p.g.c. will replace mass-spectroscopy-gas chromatography, and as usually is the case with apparently competitive techniques, one may well complement the other.

Analysis of volatile materials by p.g.c. has several advantages over the analysis of non volatile materials using p.g.c. These are:

- (1) The experimental results obtained may be compared to a theoretical model which is known to be at least qualita-







tively correct.

- (2) Pyrolysis conditions in the vapor phase may be more rigorously controlled, measured and reproduced than in the solid phase.

Several workers have published data on the pyrolysis of hydrocarbons, which has received the most attention. Keulmans and Perry (14) investigated the cracking of hydrocarbons in a quartz reactor. Sutton and Harris (18,19,20) investigated the effect of several reaction parameters and suggested optimum temperatures for the pyrolysis of several hydrocarbons.

Fanter, Wolf and Walker (7) pyrolyzed several hydrocarbons in a gold reactor and suggested a systematic method for reporting pyrolysis data based on the system used in mass spectroscopy data reporting. In this method the products of pyrolysis between stated intervals are grouped together, according to retention index, and then the normalized mole areas of the peaks found in each interval are reported.

Goforth (9) discussed reactor design for a rapid p.g.c. system using a quartz reactor. Cramers (2) discusses some design considerations for a gold tubing reactor and the kinetics of pyrolysis. Wolf and Rosie (23) studied the effect of temperature on the vapour phase pyrolysis of 20 different hydrocarbons. Gray (10) investigated the effect of variable temperature pyrolyzers on the pyrolysis of some hydrocarbons.



## 1.2 Characteristics of a P.G.C. System

When a compound is pyrolyzed it is fragmented into other compounds which are usually smaller than and more unsaturated than the parent.

The fragmentation pattern, ideally, is characteristic of the parent; and thus by identifying the fragments identification of the parent may be made.

Since the fragments are volatile they may be analyzed by gas chromatography which is ideal for this type of analysis for the following reasons:

- (1) Separation - Gas chromatography is the best method that can offer the separating power needed to enable a detailed analysis of all the fragments.
- (2) Fingerprint - The chromatogram of the decomposition products of a compound can be used for identification by comparing with "pyrograms" from known compounds.
- (3) Product Analysis - Identification of the degradation products is often possible using retention data. Collection of fragments at the column outlet allows further investigation by spectroscopic methods.
- (4) Small Sample Size Requirements - Samples of 1  $\mu$ g and less may be analyzed.
- (5) Economy - The combination of pyrolysis and gas chromatography is relatively inexpensive, hence its reputation as "poor man's mass-spectrometer".

Thus a system as shown schematically in Fig. 1.1 can be used to separate and identify each peak from the first



chromatograph.

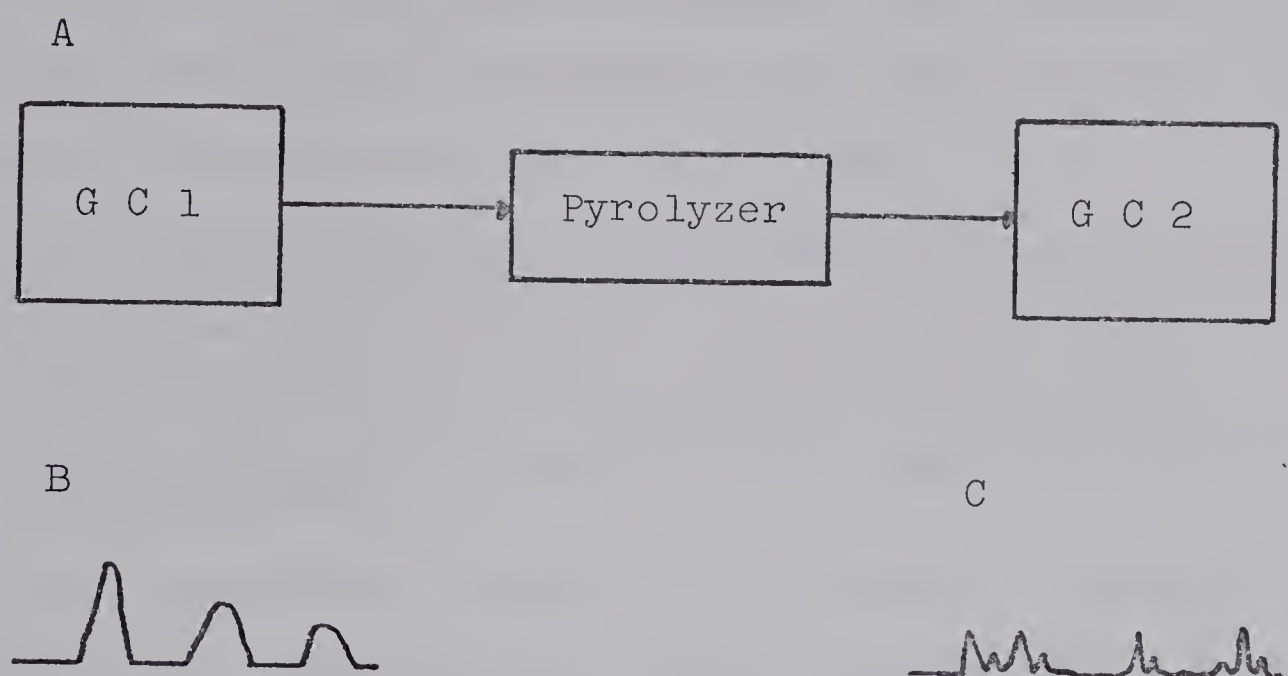


Fig. 1.1 Schematic diagram of a P.G.C. system for the separation and identification of a mixture  
 A Block diagram for the system  
 B Recorder output of g.c. 1  
 C Recorder output of the analytical g.c. (g.c. 2)

Until recently it was difficult to interpret a pyrogram in an absolute manner, since factors such as reactor temperatures and residence time can change the product distribution considerably. The normal practice was to compare the pyrogram of the unknown with pyrograms of known compounds. Since each compound has a characteristic fragmentation pattern identification could be made.

Brown (1), by means of working rules and correlations





has shown that it is possible to interpret the pyrograms of alkanes in an absolute manner. He shows by giving several examples how it is possible to interpret the pyrogram to obtain the identity of the unknown using these working rules. He states in the introduction of his paper

This study demonstrates that monoolefins from thermal degradation are characteristic of the starting alkane structure. This behavior can be used to predict accurately the structure of the original alkane. For the alkanes, then, pyrolysis gas chromatography has advanced beyond the capability of identification by comparison only.

The fragmentation pattern of an alkane on thermal degradation is independent of reaction temperature and residence time. The % composition of the olefins produced by fragmentation varies considerably with variations in reaction conditions. To obtain pyrograms which are useful in identification one must know some requirements of a P.G.C. system.

- (1) Olefins such as ethylene, propylene and alkanes such as methane, ethane and propane are produced by nearly all organic compounds when they are thermally degraded. They are therefore of minimal diagnostic value. Olefins which are most useful as diagnostic "tell tale" olefins are produced by careful selection of reaction conditions.
- (2) The sample size should be as small as possible and yet be large enough to yield measurable and identifiable peaks on pyrolysis. When the sample size becomes too large secondary reactions occur and recombination products (14) such as benzene, toluene and xylene, which are of minimal diagnostic value, are formed from the





pyrolysis of alkanes. The optimum sample size is such that there is no more than one sample molecule per thousand molecules of carrier gas... this is slightly less than one microlitre of sample with normal carrier gas flow rates (10). To obtain measurable peaks with sample sizes of less than one microlitre it is necessary to have almost 100% pyrolysis. Thus it is necessary to use high temperatures.

- (3) The reactor should be versatile enough to be used to pyrolyse a wide range of compounds without involving expensive and time consuming changes to equipment.

Some of these requirements are non compatible and therefore compromises are adopted. Each worker builds his own reactor to suit his particular needs. The reactor built is usually operated isothermally although variable temperature pyrolyzers have been used (10).

Many materials have been used to build pyrolyzers including steel, copper, quartz and gold. The latter seems to be the most popular. The pyrolysis chamber is sometimes left unpacked particularly if the gold tubing reactor is used. Quartz reactors tend to be packed. Packing has several advantages (18):

- (1) It gives a better temperature profile for the reactor.
- (2) It permits intimate contact of the sample molecules with the heated surface.

A wide variety of packing materials have been used including Chrombsorb P (6), quartz wool (17) and glass beads (19).



No systematic investigation of the effect of reactor packing material on the extent of pyrolysis and the pyrolysis pattern of the alkanes has been published. It may be possible that by selection of a good packing material to obtain useful pyrograms, i.e., ones with large amounts of "tell tale" olefins using high temperatures and short residence times.



## CHAPTER II

### REACTOR DESIGN AND PACKING SELECTION

#### 2.1 General Considerations

Construction of a pyrolysis device is a relatively simple task, which has encouraged many workers in the field to design their own units or to modify units previously described by others. The number of units described so far in the literature, therefore, almost equals the number of publications dealing with the technique.

Levy (18) states in his excellent review of pyrolysis gas chromatography. In fact almost any reactor can be used to produce a characteristic fingerprint, which can be compared with fingerprints obtained from standard substances. The variety of solid phase pyrolysis units in particular hampers possible compilation of P.G.C. data for interlaboratory use.

In vapor phase pyrolysis, however, the parameters which control the thermal reaction are well defined. In this situation a thermal degradation carried out under exactly known conditions must lead to reproducible cracking patterns. Therefore, a reactor should permit accurate temperature and reaction time control. Data obtained from such a device can also be used for the study of the mechanism and kinetics of thermal degradation. Two types of reactors, batch and flow through reactors are used to study thermal degradation reactions.

Flow through reactors are used for reactions having



short half life reaction times and may be used in a system such as shown schematically in Fig. 1.1 in which the reactor is applied to the identification of peaks eluting from a separatory column.

Thus a flow through reactor is needed for vapor phase pyrolysis which permits accurate, rigorous temperature and residence time control.

## 2.2 Reactor Design Considerations

In designing a reactor it has to be considered what is the purpose of the project. One design which may suit one project may not be the best for another project. This makes standardization of reactor design difficult.

Having established the goal of the project it should be possible to design an ideal reactor for this purpose. However the design is influenced by so many factors that it is inevitable that compromises with ideality must be made to achieve a practical design. However if a reactor is designed carefully these compromises can be made to have a minimum effect on reactor performance.

Some of the basic factors which affect reactor performance and which should be taken into consideration when designing a reactor are the physical dimensions of the reactor, material of construction, temperature, temperature profile, residence time and reactor packing material. One further consideration is necessary. The reactor should be designed so that it can fit into the space between the sepa-





ratory gas chromatograph and the analytical gas chromatograph. In this work this is not a factor to be considered since there is no separatory gas chromatograph.

### 2.2.1 Physical Dimensions

If we consider the reactor as an extended sample injection port, then some of the physical requirements of a sample injection port will be those for a reactor.

An injection port needs to have a minimum pre-column dead space. This is because pre-column dead space (p.c.d.s.) leads to sample spreading by longitudinal diffusion and exponential dilution. This affects column performance as the sample is no longer introduced onto the column as a sharp zone but as a diffuse band. The resultant chromatogram may have overlapping peaks which, given no pre-column dead space, may have been resolved. Thus a reactor should be designed to have a minimum of pre-column dead space.

Temperature programming has made this problem less important than it was, since this technique allows longer injection times (broader initial sample band) and thus the pre-column dead space problem becomes less critical than before. However even with this development it is better to keep the pre-column dead space to a minimum, for in this way the analytical g.c. system may be kept as simple as possible. For example a shorter length of column may be used or the temperature programme restricted to a small temperature range.



The best reactor is a reactor with a large length to diameter ratio (i.e., a long narrow tube) (2,9). Goforth and Cramers, independently, calculated that the ideal square temperature profile is best approximated by a small diameter tubular reactor. This result is not unexpected since this is the shape which would assure the fastest temperature equilibration with the hot walls of the reactor.

Even though a long narrow tube is the ideal, it could be advantageous in certain circumstances to sacrifice some of this idealality. A reactor with a large length to diameter ratio also has a large area to volume ratio. The large surface area therefore assures that catalytic or other effects if significant, will be amplified (2,10). The result would be a fragmentation pattern that was partly due to catalysis rather than pyrolysis due to thermal fragmentation alone. Since impurities change the catalytic effect considerably, reproducibility may be difficult. For this reason it was deemed desirable to avoid narrow diameter pyrolysis tubes.

It should also be considered that the reactor is a pre-analytical column attachment and it may be necessary to contain either its bulk or length to fit into the pre-column space available. Thus the reactor size is determined by the size of the space into which it is to fit.

### 2.2.2 Materials of Construction

The prime requirement of a material to be used for reactor construction is high temperature stability. Many materials



meet this requirement and many have been used as reactor materials.

The material should also be fairly easily obtainable, malleable and ductile. This precludes the use of some materials which meet the primary requirement of high temperature stability.

It is also desirable that the material be non catalytic. This is because catalysis affects the extent of the pyrolysis and the fragmentation pattern, and makes reproducibility difficult.

Two materials that appear to meet all the requirements are quartz and gold. Gold has been reported (2) as the best material of construction and has been used extensively. Gold however has several disadvantages. It's high cost may prevent its widespread use. Hydrocarbon pyrolysis leads in time to a carbon deposit on the walls of the reactor, this coating must be removed, either by cleaning or replacing the tube. The former is difficult, the latter expensive, although by using a combination of high temperatures and oxygen it should be possible to remove the carbon film.

Furthermore if the reactor design demands a heating system which involves wrapping resistance wire around the reactor, the insulation must be provided between the wire and the gold wall of the reactor. Unless this insulation is uniform, temperature gradients will be set up in the reactor.

Quartz is cheaper, easily available in a wide variety of lengths and tube diameters. Since the present work de-





mands the use of more than one reactor tube, quartz was chosen as the material of construction.

### 2.2.3 Temperature and Temperature Profiles

The ideal temperature profile for an isothermal reactor is a square profile, see Fig. 2.1. In practice this can only be approximated since it is impossible to change the temperature instantaneously. The flow rate of the carrier gas, the physical dimensions of the reactor, the presence of packing, and the method of heating affect the squareness of the profile.

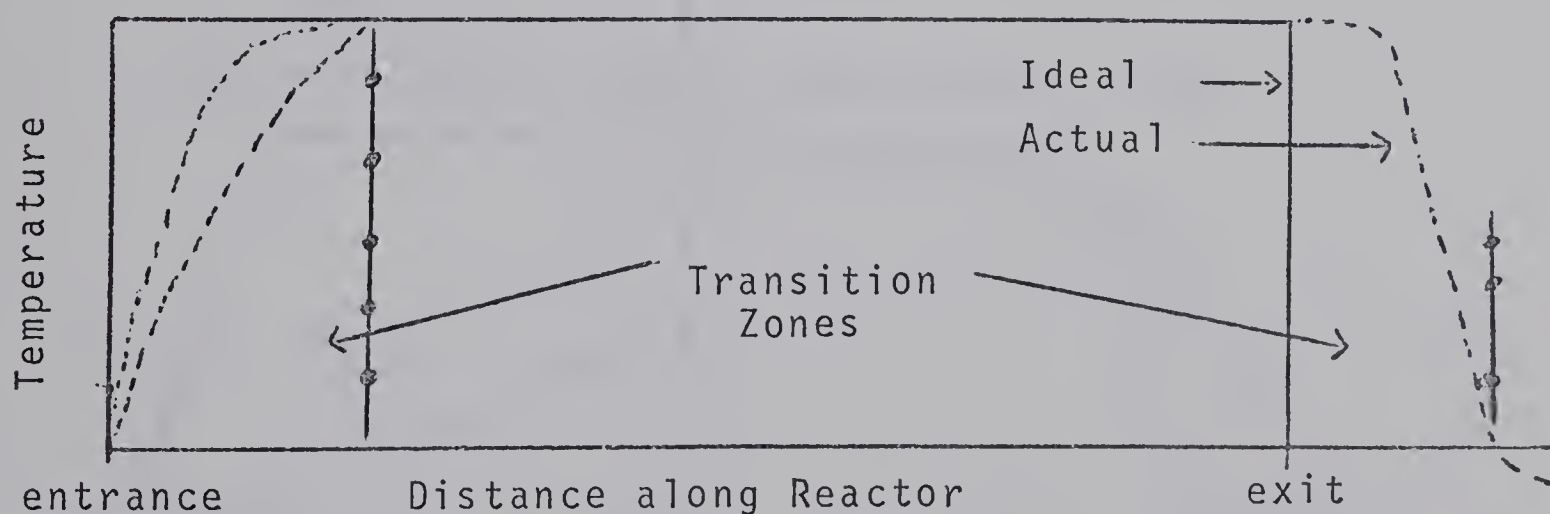


Fig. 2.1 Idealized temperature profile for an isothermal reactor showing how actual profile differs from ideal profile

According to Levy (18) the flow rate should be low since high flow rates tend to distort the temperature distance profile, Fig. 2.2B, although this effect is minimized by the use of small diameter tubes. The expected variation of the





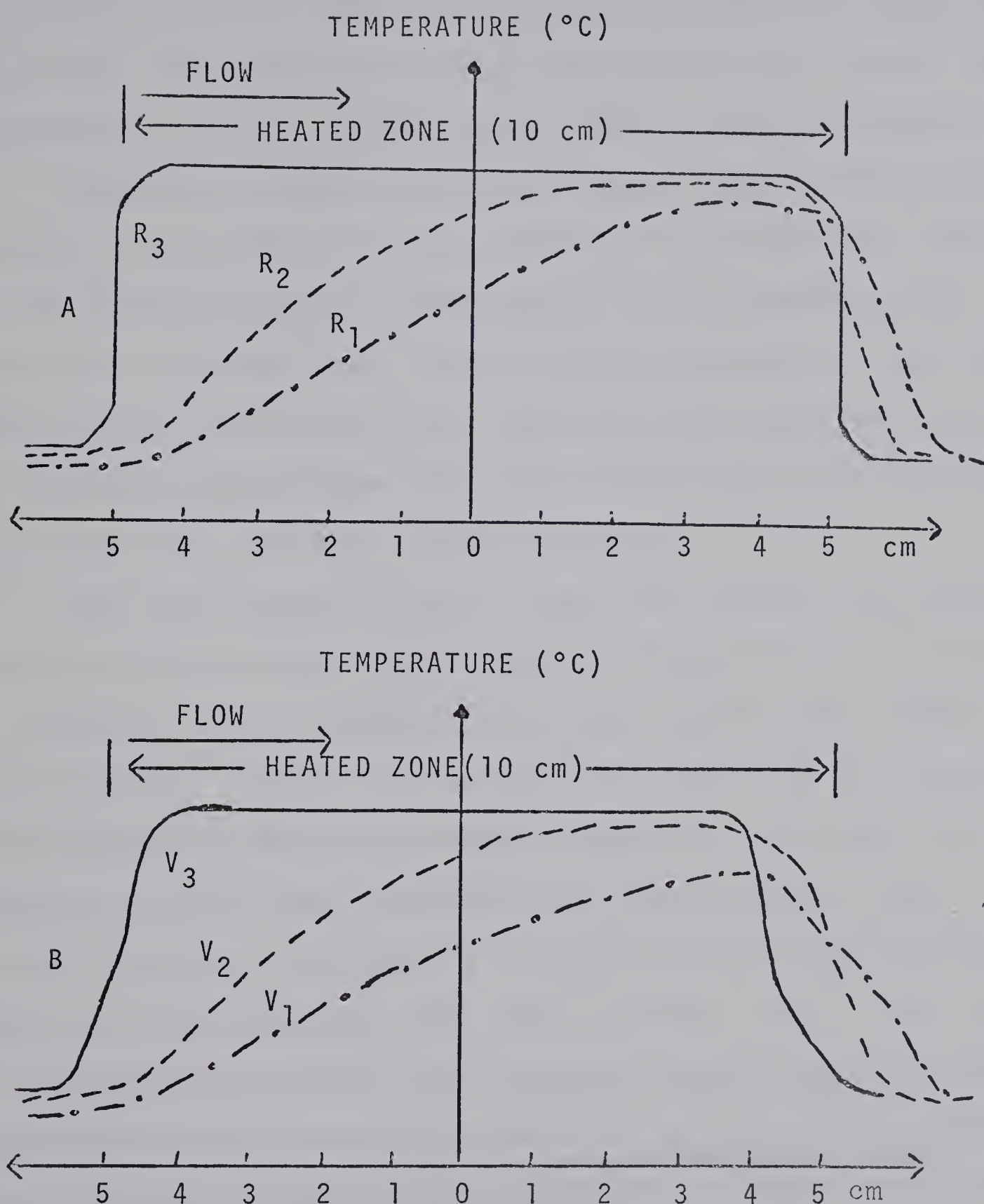


Fig. 2.2 Schematic presentation of expected temperature profiles along the axis of externally heated cylindrical microreactors. A. Expected profiles of microreactors of different internal diameters ( $R_1 > R_2 > R_3$ ) and same linear velocity of carrier gas. B. Expected profiles of a microreactor operated at different linear velocities of the carrier gas ( $V_1 > V_2 > V_3$ ) assuming non-turbulent flow. (Copied from Levy (18)).



temperature profile with increasing tube radius is shown in Fig. 2.2A. The profile is thus supposedly "most square" for a combination of low flow rate and small diameter tubing.

Goforth (9) however, found that the temperature time profile is best (that is, the ratio of the transition time to the residence time is the lowest) for a combination of high flow rates and long, small diameter reactors. He also warns against only using the length of the transition zone to determine the optimum flow rate, since the wrong conclusion (low flow rates are best) would be drawn.

The time the gas takes to come into thermal equilibrium with the walls of the reactor can be calculated by the method of Giddings (8) and Rummens (22) using the Einstein diffusion equation. Using this method it is possible to calculate a tube diameter which will assure that the time taken for heat transfer will be small compared with the residence time. It is then necessary to design a reactor so that the transition zones are small compared with the residence time. This can be done either by making the constant temperature zone large compared with the transition zones; or using a heating method that has a sharp temperature front; or by a combination of those methods. Some compromise is necessary here since the length of the constant temperature zone cannot be increased without affecting other reaction parameters (i.e., residence time).

The method used to heat the reactor can also influence the temperature profile. If the reactor is immersed in a



furnace or heated by some other method which gives a sharp temperature front, the temperature profile will approach squareness. For the temperature front to be sharp no prior heating of the gas should take place before the reactor. At the entrance of the reactor the temperature should be raised to the desired pyrolysis temperature.

A wire wound reactor gives broadened transition zones, the reactor temperature does not increase as rapidly as in a furnace reactor. The reason for this is that the ends of the wire coil tend to get stretched slightly more at the ends than the middle of the coil does, thus the coil density at the ends is less and the temperature is lower.

There is no such thing as an ideal pyrolysis temperature. Optimum conditions are a compromise between temperature and residence times. However at high temperatures products such as methane and ethylene, which are of little diagnostic value, tend to predominate more strongly relative to other products.

Regardless of what temperature is used, the temperature must be accurately known, easily monitored and reproduced. This is easily accomplished in a good furnace reactor but can present difficulties in a wire wound reactor.

The temperature profile may be made more square by the use of packing in the reactor (18). The non-ideal temperature profile shown in Fig. 2.1 may be used to advantage. Since the temperature does not instantaneously fall from reactor temperature it may be used to prevent "cold





spots" in the connections between the reactor and the analytical gas chromatograph.

#### 2.2.4 Residence Time

Another important factor, one which affects the extent of pyrolysis and the pyrolysis pattern is the residence time. This time should be accurately known, controlled and easily reproduced.

Data in the literature tends to fall into two broad groups. Data obtained using a residence time of less than two seconds, and that obtained using residence times in the area of 6-30 secs.

Sutton and Harris (20,21) found that long residence times give the best results in terms of useful olefins for identification produced.

To control the residence time rigorously it is necessary to control the flow rate rigorously. Long residence times require either long pyrolysis tubes or small flow rates of carrier gas.

The first requirement means that the reactor may become bulky or cumbersome and objections to this type of reactor are to be found in the section dealing with physical dimensions.

Low flow rates often mean that the analytical gas chromatograph is not operating under optimum conditions, with low flow rates we are in the steeply rising part of the Van Deemter curve, this is undesirable since it is necessary





to have a good separation of pyrolysis products for identification purposes.

Most of the data in the literature has been obtained using short residence times, thus workers have sacrificed the performance of the reactor in order to operate the analytical gas chromatograph at optimum conditions.

Goforth (9) and Gray (10) used a system whereby it was possible to control the flow through the reactor and analytical column separately. Thus, both may be operated under optimum conditions. With the flow through the reactor known and controlled it is possible to calculate the time spent in the reactor (residence time).

### 2.3 Reactor Design for Vapor Phase Pyrolysis

From the discussion in the previous sections an ideal reactor would be one made of gold heated in a furnace with no heating prior to the furnace. The flow through the reactor would be controlled independently of the flow through the analytical column (additive flow method). This system may be seen schematically in Fig. 2.3.

However, in the present work, some deviations from ideality were made in order to achieve a workable inexpensive system.

The additive flow method was used in the first few experiments but difficulty with the method was found. The measurement of the flow through the reactor was found to be more difficult than suggested by Gray (10) and Goforth (9).



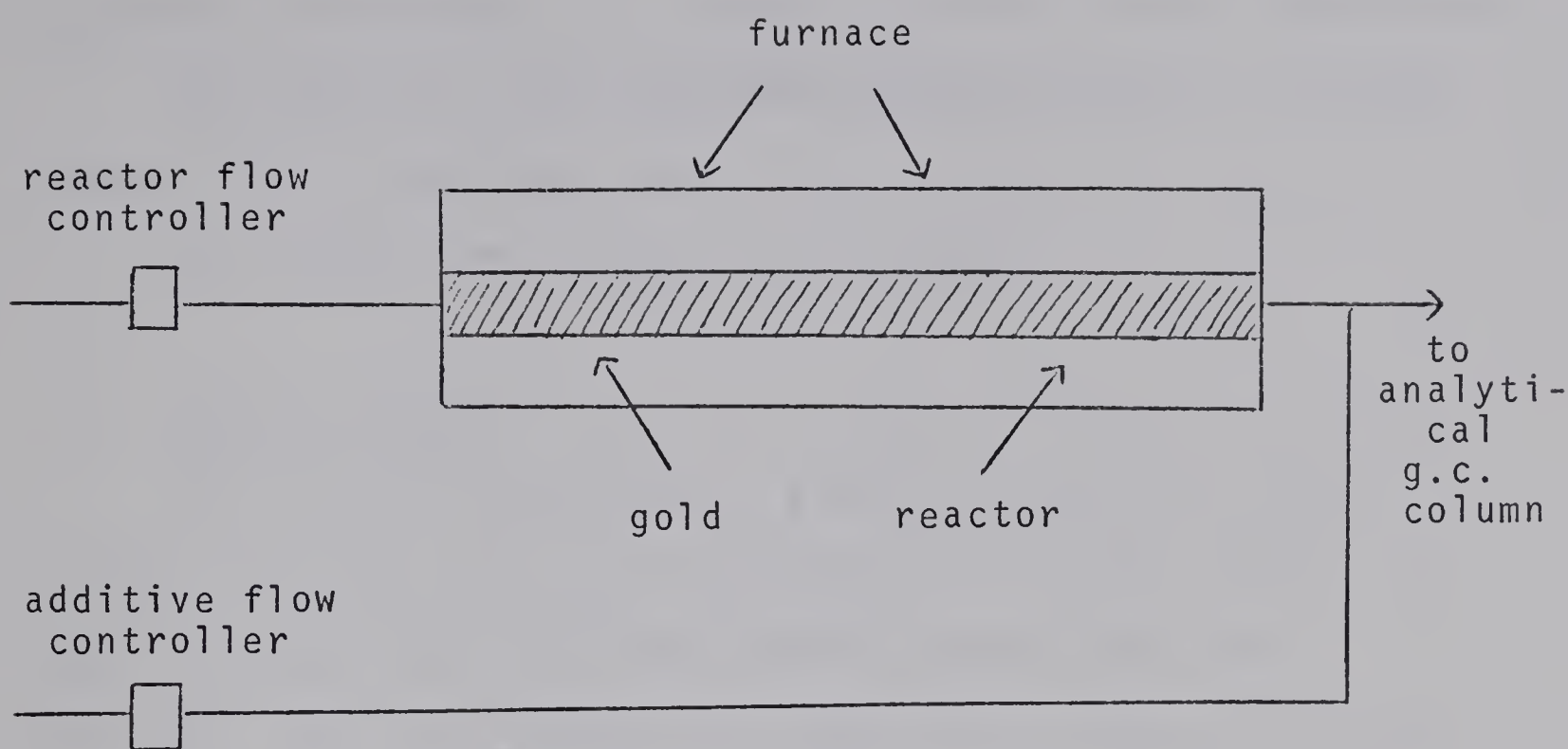


Fig. 2.3 A schematic diagram showing a reactor system with independent control of flow rate and pyrolysis time

However the main difficulty was found in trying to get steady low flow rates. A typical reactor used had a pre-column dead space of one cubic centimeter. For a residence time of 6 seconds, this means that the flow rate has to be of the order of 10 ml/minute. The back pressure of the reactor is around 8 p.s.i. For the flow controllers to control the flow independent of fluctuations in downstream pressure the difference between inlet and outlet pressure needs to be 50 p.s.i. This means that the inlet pressure into the valve needs to have a value of 65-60 p.s.i. since the analytical column has a back pressure of 6 p.s.i. To obtain reproducible flow rates of the order of 10 ml/min. using a tank pressure of 70 psi proved to be difficult; for



residence times above 6 seconds it proved almost impossible.

The additive flow method was abandoned and a straight through flow system was used.

The reactor was heated in a furnace.

## 2.4 Furnace Design

The furnace consisted of a quartz tube 52 cm long, 16 mm in diameter was wound around 50 cm of this tube. A layer of Fibrefray Insulation 9703 (Carborundum Ltd., Ontario). This was secured to the tube by means of strips of sticky fibreglass tape (3M Company Ltd.). The heating element was wrapped onto this insulation. The element was made of 1/8th inch wide Chromel No. 36 wire having a resistance of 1.06 ohms per foot. The element was held in place by sticky fibreglass tape. This construction was then baked for 12 hours at 1,000°C in a fume hood. This is done to prevent shorts in the insulation.

Triple layers of Fibrefray Insulation 9703 were wrapped around the tube, each one was secured by fibreglass tape before wrapping the next layer.

Then two layers of Aluminized Fibreglass Firetex were wrapped around the tube then secured. Finally, fibreglass tape was wrapped around the tube to secure all the layers.

The furnace was baked at 1,000°C (for 12 hours) to remove volatile components. It was then ready for use.

The element was silver soldered to the wires leading to the two mode controller.





#### 2.4.1 Temperature Control of Furnace

The temperature of the furnace was controlled using an A.P.I. two mode controller. The thermocouple used was Iron/Constantan.

The specifications given for the controller states that the controller will control to  $\pm 0.5^{\circ}\text{C}$ . The temperature of the furnace was monitored using a chrome-alumel thermocouple, which was inserted between the walls of the furnace and the wall of the reactor.

At each end of the furnace there was a one cm-non insulated, non heated zone. This was included to prevent melting of the teflon tape used to seal the reactor. In this one cm length a transite block was placed to keep the reactor in the center of the furnace and to reduce heat losses.

#### 2.4.2 Reactor Design

The reactor consisted of a quartz tube 57 cm long and 6 mm in diameter. The heated portion of the reactor tube, 50 cm, was packed with the desired packing material. A plug of quartz wool was inserted into each end to prevent the packing from falling out.

The reactor was kept in the centre of the furnace by Transite blocks as shown in Fig. 2.4. The Transite blocks were constructed as shown in Fig. 2.5 and served two purposes, namely to hold the reactor tube in the center and to prevent heat losses.





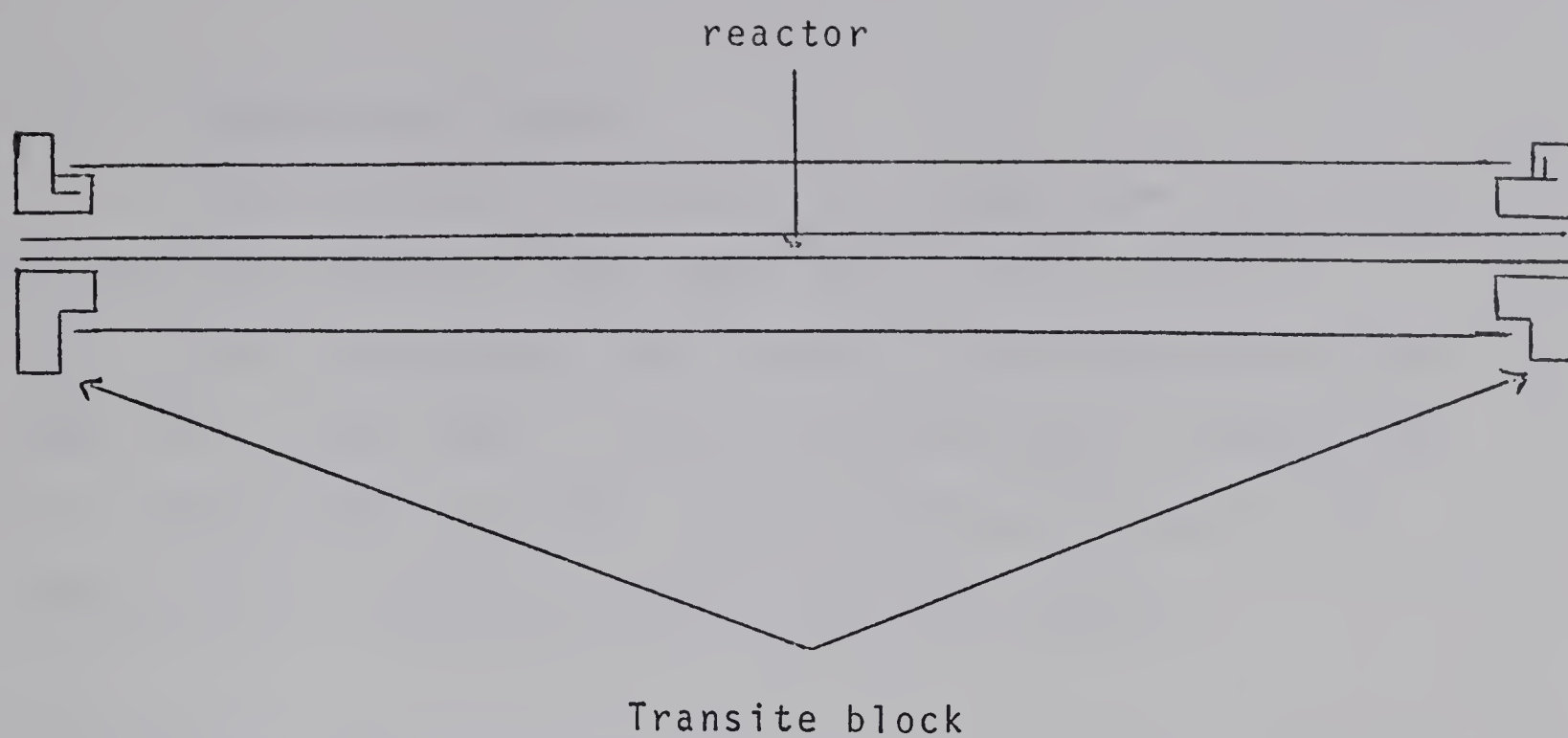
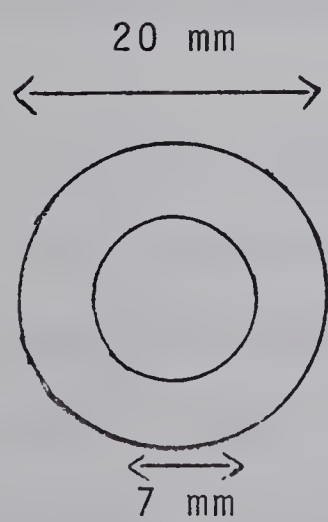
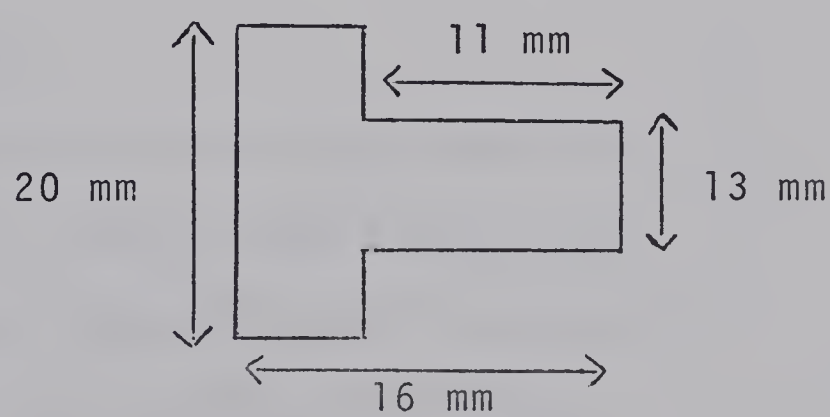


Fig. 2.4 Diagram showing position and function of Transite blocks



front view



side view

Fig. 2.5 Design of Transite blocks



### 2.4.3 Temperature Profile

It was possible to measure the temperature profile of the packed column, so the temperature profile shown in Fig. 2.6 of the reactor tube is that of an unpacked reactor tube with no gas flow. The profile was drawn by insertion of a thermocouple into the reactor tube and measuring the temperature at various lengths along the reactor.

### 2.4.4 Reactor Connections

#### 2.4.4.1 Analytical Column End

Teflon tape was wrapped around the reactors to increase the diameter of the tube so that 1/4 inch Swagelock fittings could be used. The reactor was attached to the 1/4 inch end of a 1/4 inch to 1/8 inch reducing union, the other end of the union being attached to the analytical column.

#### 2.4.4.2 Injection Port End

The injection port consisted of a hollowed out 1/4 inch Swagelock tee. At a point 1 1/2 cm from the end of the reactor tube Teflon tape was wrapped around the reactor to increase its diameter so 1/4 inch Swagelock fittings could be used. The Swagelock fittings were placed on the tape and connected to the tee. The reactor tube was allowed to protrude into the tee fitting for two reasons:

- (a) It permitted the syringe carrying the sample <sup>done</sup> to be inserted well into the reactor tube <sup>done</sup>, thus acting as a syringe guide.



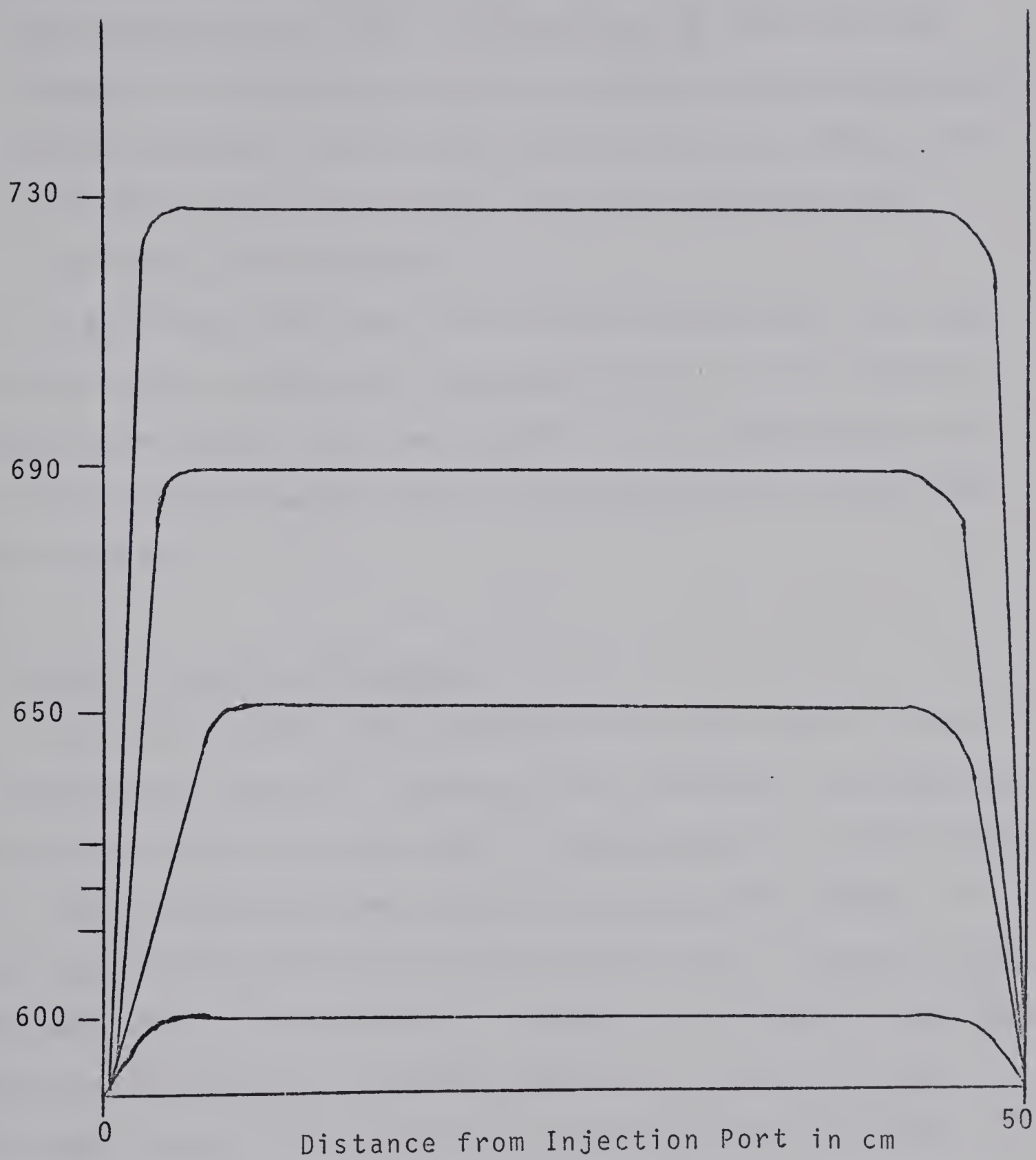


Fig. 2.6 Temperature profile in an unpacked reactor tube



(b) In an injection port made of a Swagelock tee there is gas turbulence at the 'T' junction. By ensuring the sample in the syringe does not encounter this turbulence, sharp injection front could be obtained, as compared to a diffuse one of the sample had been injected under conditions of turbulence.

A guide was also made, and placed between the 1/4 inch nut holding the septum and the septum to ensure the syringe injected the sample into the reactor. This guide consisted of a 1/8 inch brass back ferrule superimposed on a 3/16 inch front ferrule.

## 2.5 Reactor Packing Selection

Levy (18) states that packing a reactor should improve its temperature profile. Despite this statement the majority of pyrolysis work has been done in empty quartz or gold tubes.

There have been some studies using packed columns, in these cases Chromsorb P (6), quartz wool (17), or glass beads (19), were used as the packing. However no systematic investigation on the effect of packing material on pyrolysis has been done. Levy (18) states that a packing material like Chromsorb W may exhibit catalytic effects on the course of pyrolytic reactions in the reactor. Hence we chose Chromsorb W to see if it had a catalytic effect on the reaction. In some applications (4,5,6) these catalytic effects may prove desirable, even though possible deposition of polymerized material on the surface of the packing material may change





its catalytic properties leading to poor reproducibility.

Hence Chromsorb W was chosen as one of the packings.

Quartz wool was also chosen because it has been used in a previous study (17), and it should be possible to correlate these findings with the ones obtained in this study.

Iron metal was chosen as a packing because of its potentiality to be a non catalytic surface, so that the pyrolysis obtained would be non catalytic.

The iron coated Chromsorb W reactor was chosen to determine the effect of deposition on the surface of a catalytical material. It was made by dissolving 8.7 g of Ferric chloride in water and coating 50 g of Chromsorb W as one would normally coat a packing material. The coated packing was then heated to convert the chloride to the oxide. The oxide was then placed in a reduction boat and this was placed in a stream of hydrogen in a furnace. The resultant iron coated Chromsorb W was then ready for use.

It was assumed that iron is non catalytic, and that pyrolysis on an iron surface is due to heat alone, then the iron coated chromsorb should show the effect of deposition on a catalytical surface.

Graphite was chosen because it, too, has a potentiality for being a non catalytic surface.

## 2.6 Selection of Reactor Construction Material

The majority of the work was done using a quartz walled reactor.



However one set of data was obtained using a graphite packed steel reactor. This was to determine the effect of changing the reactor material on pyrolysis. Comparisons were made with the graphite packed quartz reactor.

Steel was chosen because other workers have found that steel is a satisfactory material of construction showing little catalytic activity. Quartz reactors tend to break easily, and so a non-breakable, inexpensive, material of construction would be desirable.

## 2.7 Method of Operation of Reactor

The reactor tube was conditioned at 750°C for 12 hours before use, a flow of helium was maintained during this time.

The reactor was kept at the reaction temperature for 30 minutes prior to injection of samples.

The samples were injected into the p.g.c. system in the order 2,3-dimethylbutane, 2,2-dimethylbutane, hexane, each being sampled in duplicate.

All samples were reacted at 600°C, then 650, 690 and 750°C.

A schematic diagram of the system is given in Fig. 2.7

- A. Brooks flow controllers.
- B. Pyrolyzer - see Chapter II.
- C. A.P.I. two mode controller - A.P.I. Instruments Co.
- D. Programmer - Varian Aerograph Linear Temperature Programmer Model 330.



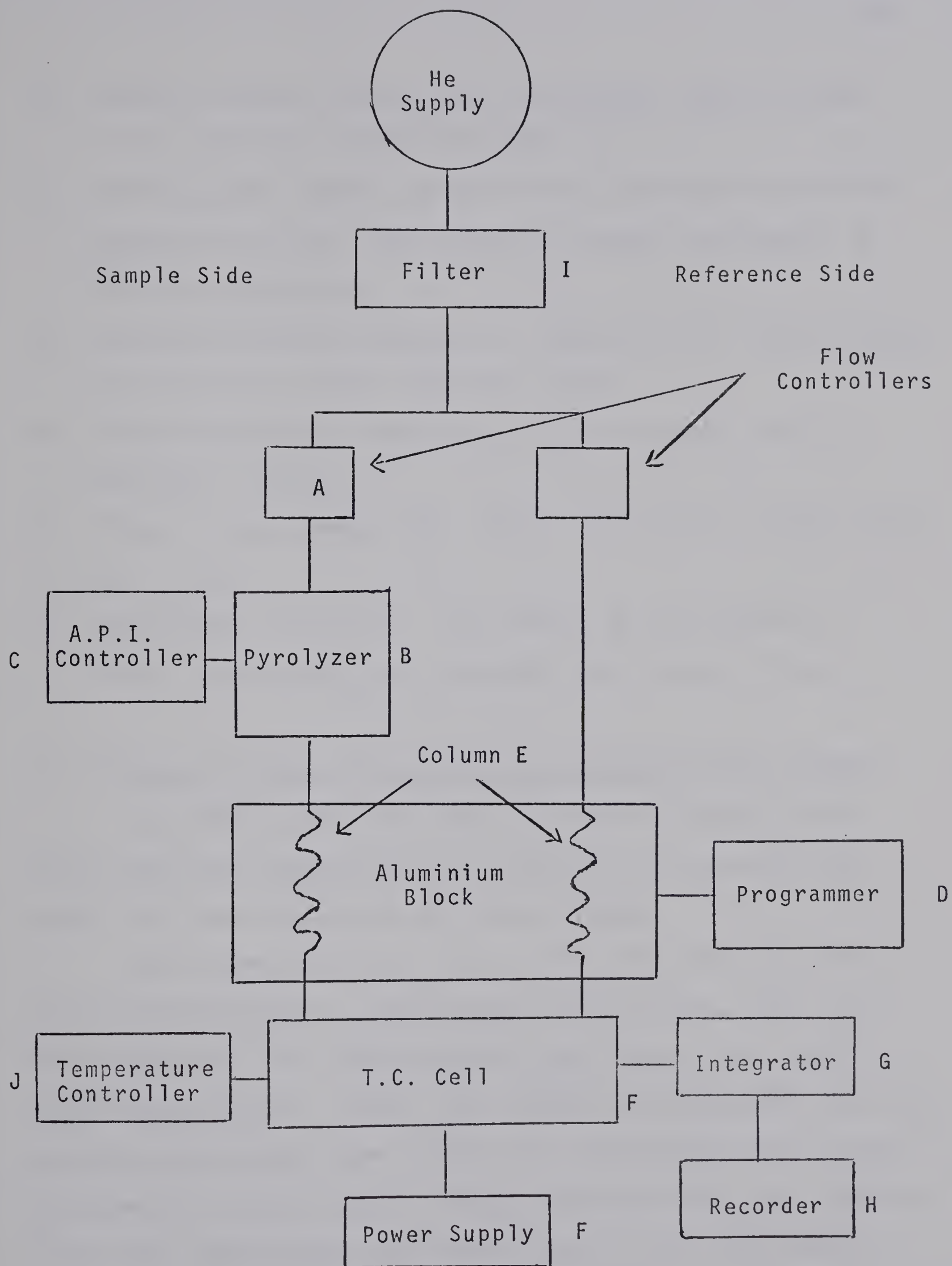


Fig. 2.7 The pyrolysis gas chromatographic system



- E. Porapak Q (Waters Associates, Framington, Mass.) column 6 ft. x 1/8 inch stainless steel.
- F. Gow-Mac power supply, model 40-05-C, and Gow-Mac thermal conductivity cell, model 9285-D, Gow-Mac Instrument Co., Madison, New Jersey.
- G. Aerograph digital integrator - model 471-42 - manufactured by Infotronics Corp., Houston, Texas.
- H. Sargent Recorder - model S.R. - E.H. Sargent and Co., Chicago, Illinois.
- I. Filter - Trap number 236 - Guild Corporation, Bethel Park, Pa., U.S.A.
- J. Temperature Controller - RFL Model 20-115/208/230 V - R.F.L. Industries, Inc., Boonton, New Jersey, U.S.A.

## 2.8 Method of Operation of the Gas Chromatographic System

In order to make the identification of parent peaks easier the gas chromatographic separation was carried out under the same conditions for every sample.

The column used was 6 ft. x 1/8 inch stainless steel, packed with Porapak Q. The initial temperature, 40°C, was maintained for five minutes after injection of the sample into the pyrolyzer. After five minutes (during which methane, ethylene and ethane were eluted) the temperature was allowed to rise at 4°C/min. until a temperature of 180°C was reached. This final temperature was maintained till all the components had been eluted, usually five minutes.

A temperature programme compensating column underwent







the same temperature programme as the sample column.

The aluminium block was cooled to the initial temperature by allowing carbon dioxide to flow through a pipe inserted in the block. This permitted rapid cooling.

The flow rates through the column were measured using a soap bubble flow meter and were corrected to 0°C and 760 mm of Hg pressure.

The pressure at the injection port of the pyrolyzer was measured using a pressure gauge supplied by Matheson.

The reference and sample side flow rates were adjusted separately, and were so adjusted that they were within 0.3% of each other.

The areas obtained from the integrator were converted to molar areas by the use of response factors.

Molar area = peak area x molar response factor.

In all calculations molar areas were used since peak area calculations give a misleading picture of product distribution.

## 2.9 Calculation of Residence Time

In order to calculate the residence time the amount of dead space in the reactor must be known. In the case of an unpacked reactor this presents no problem as the dimensions may be easily measured. This is not the case with a packed reactor, and so a method had to be developed in order to calculate the reactor dead space. In the pyrolysis gas chromatographic system used the only difference between the



dead space on the sample side and the dead space on the reference side is the dead space due to the reactor. The reference side column was fitted with an injection port similar to the one on the sample side hence any dead space difference due to the presence of an injection port on the sample side alone is eliminated.

The reactor was allowed to reach the operating temperature. 10  $\mu$ l of air was injected into the sample side and simultaneously a stop watch was started. The stop watch was stopped when the air peak reached a maximum and the time was noted. A similar experiment was carried out on the reference side. The flow rate of helium passing through the sample and reference side was measured. Then if

$t_s$  = Time required for air peak to be eluted on the sample side.

$t_r$  = Time required for air peak to be eluted on the reference side.

Then  $t_s - t_r$  must be due to the dead space of the reactor. If the flow rate of helium is  $F_0$ , the temperature of the surroundings  $T_s$  and the atmospheric pressure, the pressure inside the reactor  $P_{\text{react}}$ , the reactor temperature  $T_{\text{react}}$  and the dead space of the reactor  $V_{\text{react}}$ .

Then

$$\frac{(t_s - t_r) F_0 (P_{\text{atmos}} - P_{\text{water}})}{T_s} = \frac{P_{\text{react}} \cdot V_{\text{react}}}{T_{\text{react}}} \quad (1)$$



where  $P_{\text{water}}$  = Vapor pressure of water at  $T_s$ .

All the quantities in the above equation may be calculated except the  $V_{\text{react}}$  which is what is required.

The flow was measured at the outlet of the system using a soap bubble flow meter.

In calculating the residence time the flow rate is measured at the outlet of the system, and corrected to 273°K and one atmosphere pressure by the following equation.

$$F_m^O = F_m \frac{(P - P_w) 273}{760 T} \quad (2)$$

where  $F_m^O$  is the measured corrected flow rate

$F_m$  is the measured flow rate

$P$  is the atmospheric pressure in mm of mercury

$P_w$  is the water vapor pressure at temperature  $T$ .  
°K in mm of mercury.

The flow at the entrance to the pyrolyzer tube may be written as

$$F_0 = F_m^O \frac{P}{P_p} \quad (3)$$

where  $F_0$  is the flow at the entrance of the pyrolyzer

$P_p$  is the pressure in the pyrolyzer.

Then the residence time  $\tau$  is calculated by the equation



$$\tau = \frac{T_s P_p V_{\text{react}}}{F_m^0 T_p P} \quad (4)$$

Since all the quantities in equation (4) may be measured,  $\tau$  may be calculated.

The pressure in the reactor was measured by the use of a Johnson pressure gauge to which had been attached a pressure line and needle. This was inserted through the rubber septum. Before measuring the pressure in the reactor the reactor was disconnected from the analytical column as this exerts a considerable back pressure which will give erroneous results.





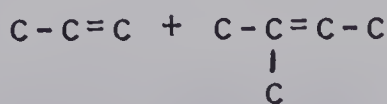
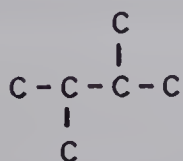
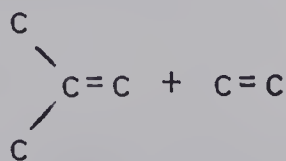
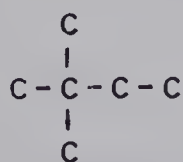
## CHAPTER III

### RESULTS AND DISCUSSION: THE SELECTION OF REACTION CONDITIONS

To study the effect of temperature, residence time and reactor packing on pyrolysis, the pyrolysis of three model compounds under various conditions was investigated.

The three model compounds chosen were hexane, 2,3-dimethylbutane and 2,2-dimethylbutane. These compounds are readily available in pure form. The breakdown pattern of the three compounds may be predicted using the Rice Kossiakoff (15) theory of pyrolysis. Table 3.1 gives the model compound structure and the major products expected on pyrolysis.

Table 3.1 The carbon skeleton of the model compounds chosen and their major pyrolysis products





Hexane gives large amounts of 2 carbon atom molecules, and some 3 carbon atom molecules on pyrolysis whereas little of 4 carbon atom or 5 carbon atom molecules is formed.

2,2-dimethylbutane gives some 4 carbon atom and some 2 carbon atom molecules but no 3 carbon atom molecules.

2,3-dimethylbutane gives 2, 3 and 5 carbon atom molecules.

The pyrolysis of these three compounds has been investigated (10), and it has been shown that the products predicted by the Rice-Kossiakoff theory are the ones that are formed.

The typical pyrograms of hexane, 2,2-dimethylbutane and 2,3-dimethylbutane are shown in Fig. 3.1, 3.2 and 3.3.

The sizes of the peaks vary considerably with different conditions. If a peak was less than 1% of total, Gray considered negligible for the purpose of the tabulation of results.

### 3.1 Methods of Normalization

In order to make meaningful comparisons of results it is necessary to normalize the results. The method of normalization chosen can have a significant effect on the superficial appearance of the results. There are three methods of normalization which yield useful comparisons and are readily calculated from the molar areas. They are:

$$\text{Normalized peak (M}_1\text{)} = \frac{\text{molar peak area}}{\text{sum of the areas of the product peak}}$$



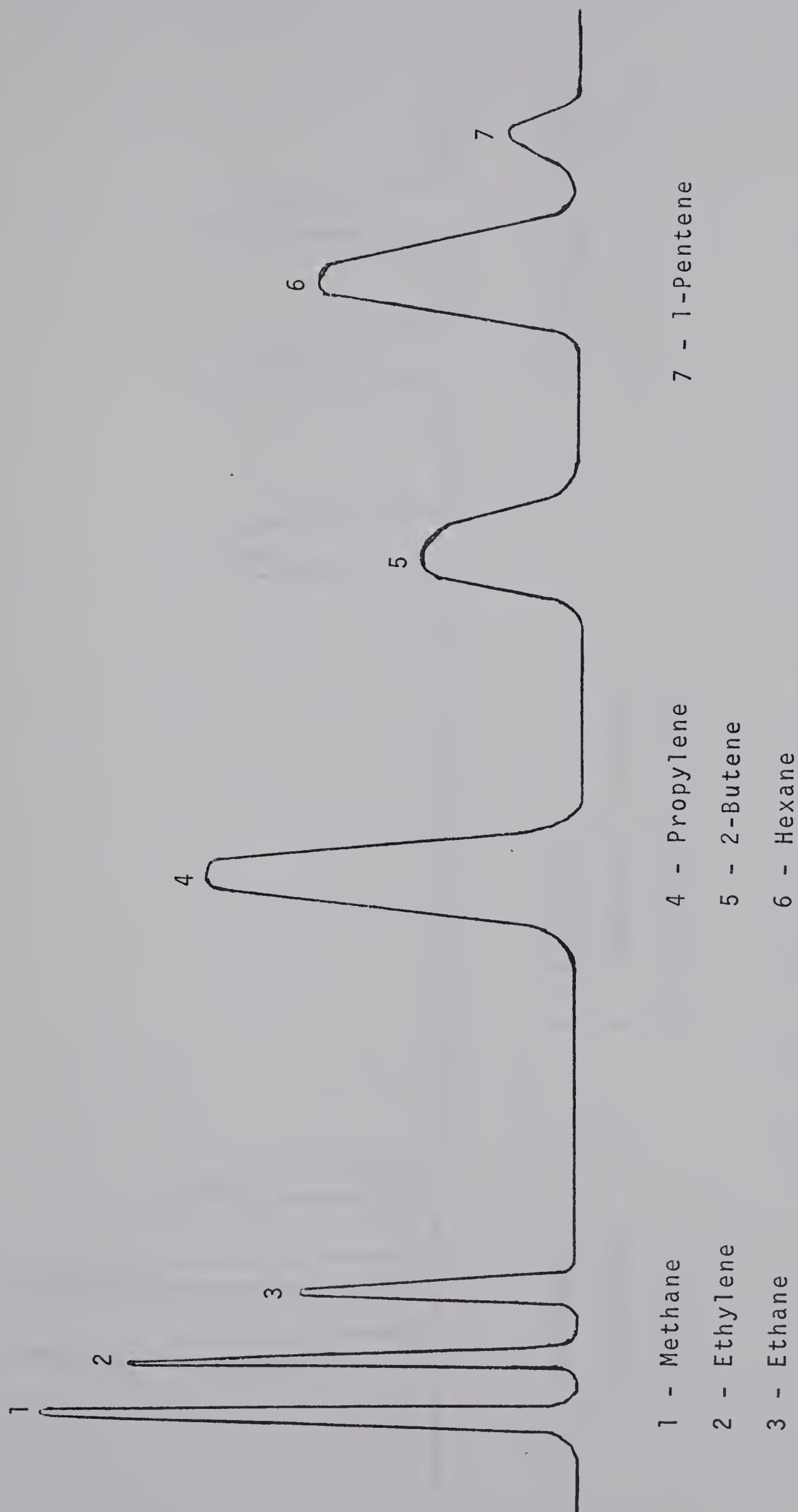


Fig. 3.1 A typical pyrogram of Hexane



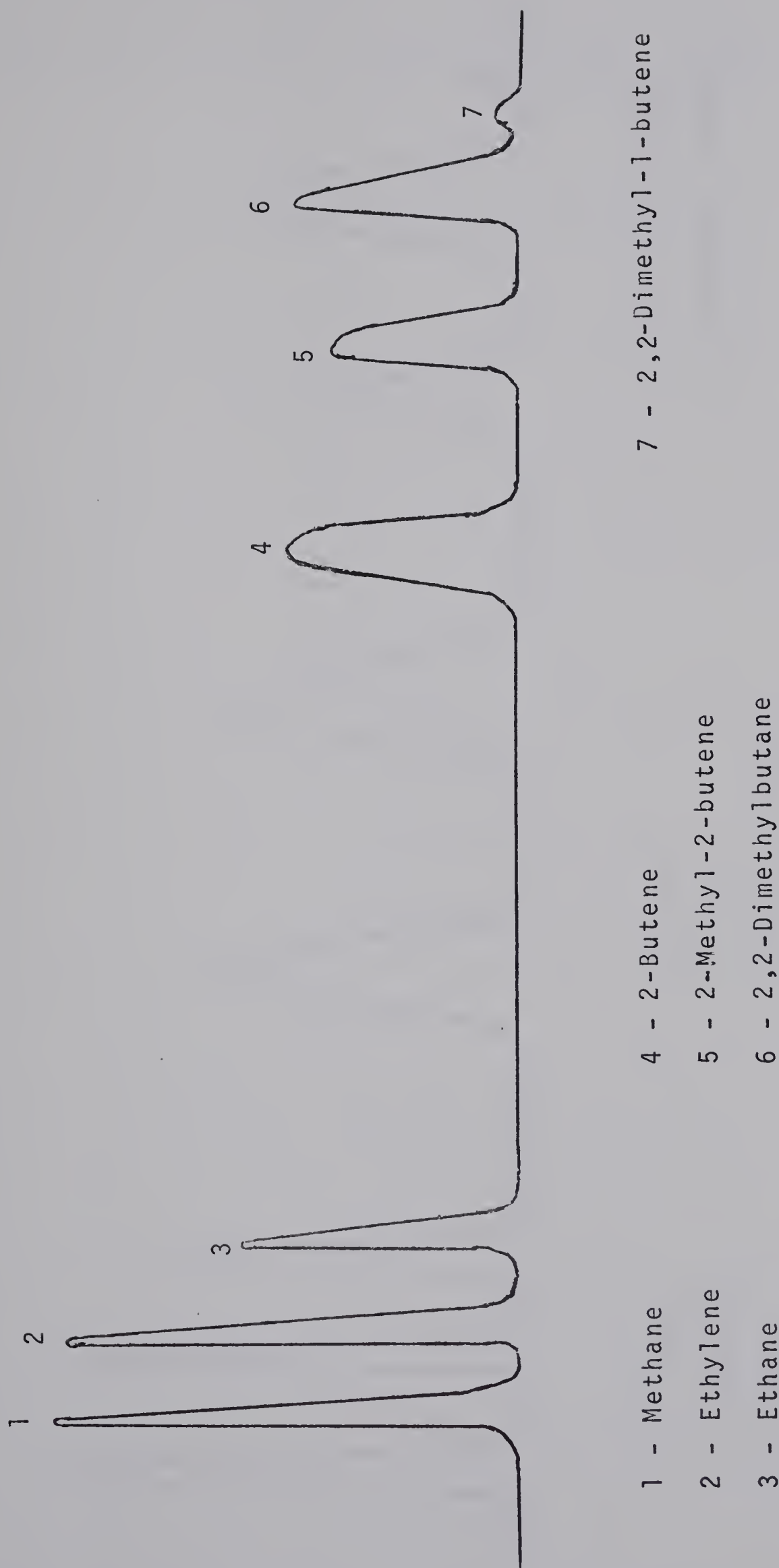


Fig. 3.2 A typical pyrogram of 2,2-dimethylbutane





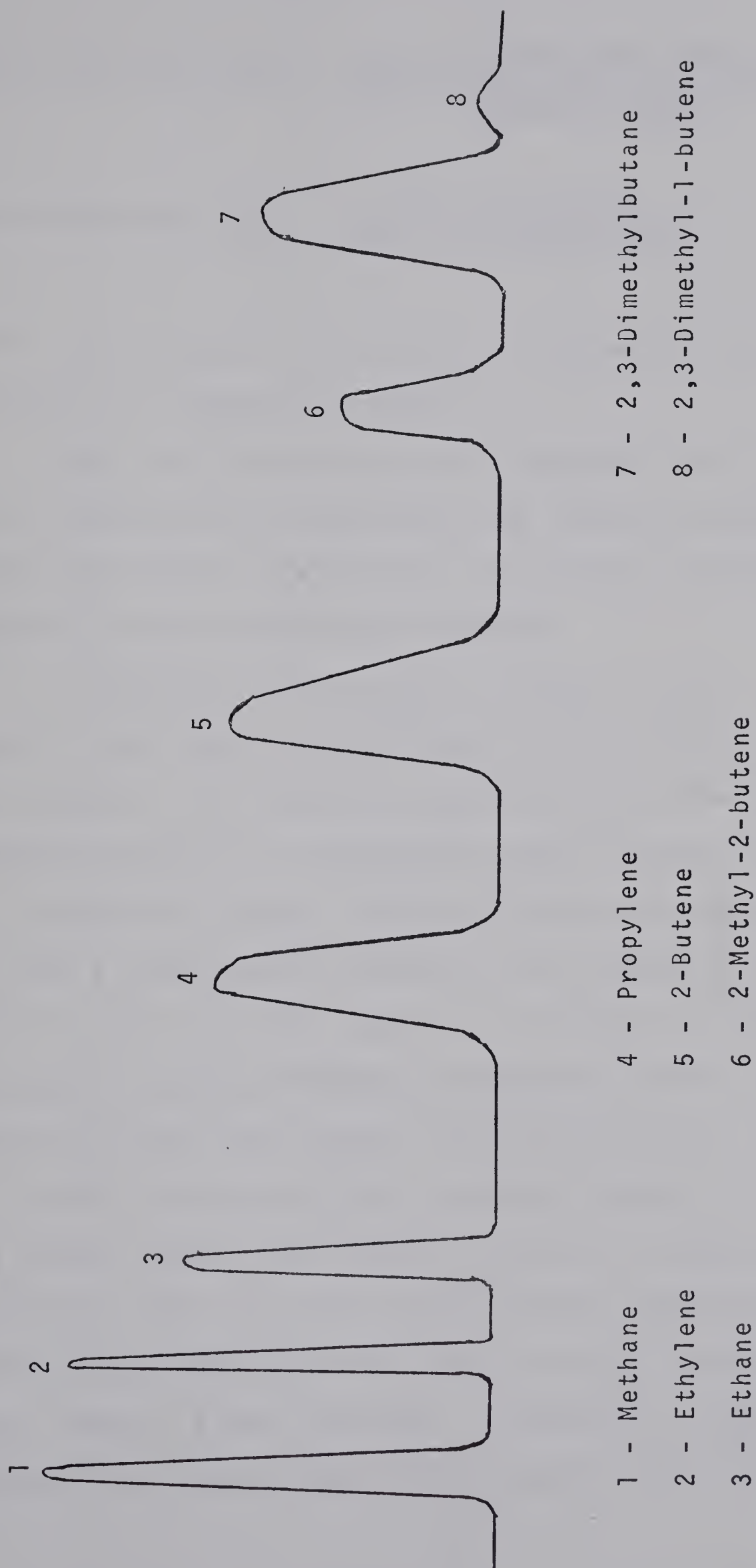


Fig. 3.3 A typical pyrogram of 2,3-dimethylbutane



$$\text{Normalized peak (M}_2\text{)} = \frac{\text{molar peak area}}{\text{sum of the areas of products and reactant peaks}}$$

$$\text{Normalized peak (M}_3\text{)} = \frac{\text{molar peak area}}{\text{area of largest peak}}$$

Molar peak areas are the areas of the peaks corrected for variation in response factors.

From the definitions it is apparent that  $M_2$  will approach  $M_1$  as the pyrolysis approaches one hundred percent. Table 3.2 shows the results of pyrolysis at several different temperatures with each of the three methods.

Using data from one set of results only, it would be easy to draw varying conclusions on the effect of temperature. For example, the results by method  $M_1$  show the amount of methane formation as remaining almost constant over most of the temperature range, whereas, the results by method  $M_2$  and  $M_3$  show a significant increase in the amount of methane formed. Similarly  $M_1$  shows the amount of 2-methyl-2-butene formed decreases steadily whereas the absolute amount increases. Method  $M_1$  shows the product distribution best; however since the amount of non pyrolyzed reactant present is omitted from the normalization the results are not all that useful. Method  $M_2$  shows the total fragmentation pattern better, comparisons are good since the total area of reactants and products remains almost constant. Method  $M_3$  is basically the same as the normalization method used in mass spectroscopy



Table 3.2 The effect of different methods of normalization on appearance of the results of the pyrolysis of 2,3-dimethylbutane

Temperature Products	600°C			650°C			690°C			750°C		
	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>
Methane	0.17	0.02	19	0.19	0.09	17	0.14	0.11	37	0.38	0.34	100
Ethylene	--	--	--	0.05	0.02	4	0.04	0.04	12	0.28	0.25	74
Ethane	--	--	--	--	--	--	0.06	0.05	17	--	--	--
Propylene	0.32	0.03	35	0.35	0.16	30	0.37	0.31	100	0.23	0.20	60
2-Butene	--	--	--	0.08	0.04	7	0.16	0.14	44	0.08	0.08	23
2-Methyl-2-butene	0.49	0.05	56	0.39	0.16	29	0.18	0.16	51	0.03	0.03	8.5
2,3-Dimethylbutane	XX	0.91	100	XX	0.53	100	XX	0.16	52	XX	0.10	29
2,3-Dimethyl-1-butene	--	--	--	--	--	--	0.04	0.04	12	--	--	--



and is the most convenient method for specifying the fragmentation pattern. Goforth (9) and Gray (10) use this method ( $M_3$ ) for reporting their results in their theses on pyrolysis gas chromatography. Cramers (2) in his thesis uses method  $M_2$  in reporting his results and Brown (1), using the results given in Cramers thesis derives his working rules. In this thesis data have been normalized using method  $M_2$ .

Another important characteristic of pyrolysis is  $\alpha$ , the degree, or extent of pyrolysis. This is calculated from the following formula.

$$\alpha = \frac{\sum_{n=1}^{n-1} c_i A_{ci}}{\sum_{n=1}^n c_i A_i} = 100$$

where  $c_i$  are the response factors of compounds  $c_i$  whose areas are  $A_{ci}$ .

### 3.2 The Effect of Temperature on Pyrolysis

The effect of temperature on pyrolysis has been investigated by several workers (10,20,23). The overall conclusion reached is that higher temperatures increase the extent of pyrolysis, providing the residence time remains constant. The pyrolysis pattern, too, is changed by temperature variations. On comparing the amount of large molecules to small molecules obtained it was noticed that this changes with





temperature. At low temperatures the formation of larger molecules predominates, whereas at high temperatures the formation of small molecules is favoured. At very high temperatures the production of small molecules is almost exclusive.

Table 3.3 gives the results of a series of experiments in which the reactor material, reactor packing and residence time were kept constant and the temperature was varied. The residence time was kept constant by changing the flow through the reactor and was calculated by the method given in Chapter II, section 2.6. The flow rate necessary to give the residence time at a particular temperature was calculated using the method given in Chapter II, section 2.6.

The reactor packing chosen was Chromsorb W, the residence time was 0.83 sec. and the material of construction of the reactor walls, quartz.

The temperatures chosen for this and other work were 600, 650, 690 and 750°C. A temperature of 750°C was chosen because, at that temperature it should be possible to study the effect of reactor packing on methane formation since methane production is most predominant at this temperature. Methane is of minimal diagnostic use. Temperatures of 650°C and 690°C were chosen because of the wide range of products formed at these temperatures. Any change in the overall pyrolysis pattern brought about by changing the reactor packing should be observed at these temperatures; 600°C was chosen because, normally little pyrolysis occurs and it may be possible to observe if, by changing the reactor packing



Table 3.3 The effect of temperature on the pyrolysis of the model compounds, other reaction parameters been kept constant  
A Pyrolysis of hexane  
B Pyrolysis of 2,2-dimethylbutane  
C Pyrolysis of 2,3-dimethylbutane

Temperature Products	600°C			650°C			690°C			750°C		
	A	B	C	A	B	C	A	B	C	A	B	C
Methylene	0.01	0.00	0.02	0.05	0.04	0.07	0.11	0.13	0.20	0.18	0.26	0.20
Ethylene	0.03	0.00	0.00	0.13	0.04	0.02	0.30	0.14	0.14	0.38	0.25	0.16
Ethane	0.00	0.00	0.00	0.03	0.00	0.02	0.05	0.10	0.16	0.07	0.21	0.19
Propylene	0.02	0.00	0.04	0.09	0.09	0.16	0.18	0.00	0.22	0.19	0.10	0.17
2-Butène	0.02	0.02	0.04	0.06	0.09	0.02	0.08	0.23	0.17	0.13	0.15	0.16
2-Methyl-2-butene	0.00	0.02	0.00	0.00	0.07	0.14	0.00	0.09	0.05	0.00	0.05	0.05
Parent	0.92	0.96	0.90	0.64	0.74	0.74	0.25	0.30	0.15	0.05	0.04	0.05
α	0.08	0.04	0.10	0.36	0.26	0.26	0.75	0.70	0.85	0.95	0.96	0.95



an increase in the extent of pyrolysis may be obtained.

From the data tabulated in Table 3.3 for the pyrolysis of 2,3-dimethylbutane the extent of pyrolysis increases from 10% at 600°C to 95% at 750°C. Similarly the extent of pyrolysis of 2,2-dimethylbutane increases from 4% at 600°C to 96% at 750°C, and hexane from 8% at 600°C to 95% at 750°C. This is in agreement with the others who have found that an increase in temperature produces an increase in the extent of pyrolysis.

To study the effect of the increase in temperature on the pyrolysis pattern a study is made of the ratio of the amount of a particular small molecule compound formed to that of a larger molecule. In the case of hexane the small molecule chosen was ethylene and the larger molecule 2-butene. The data of the table shows that at 600°C the ratio ethylene: 2-butene was 1.5:1, at 650°C 2:1, at 690°C 3.8:1 and at 750°C 3:1.

By looking at these ratios it can be seen that the temperature at which the production of the larger molecule is most favored is 600°C. As the temperature is increased the ratio changes so that at high temperatures the production of ethylene is favored even though the absolute amount of butene formed is increased at higher temperatures.

Repeating this analysis on the results of the pyrolysis 2,3-dimethylbutane and using methane as the small molecule compound and 2-butene as the large molecule compound the ratios are as follows. At 600°C the ratio methane:2-butene





was 0.5:1 at 650°C 0.5:1, at 690°C 1.1:1 and at 750°C 1.2:1.

In the pyrolysis of 2,2-dimethylbutane the ratio of methane to 2-butene changes as follows, at 600°C 0:2, at 650°C 0.5:1, at 690°C 0.7:1 and at 750°C 1.8:1. At 750°C the formation of methane, ethylene, ethane and propylene is almost exclusive.

Using the data given in Table 3.3, it is seen that an increase in temperature increases the extent of pyrolysis. As the temperature is increased the pyrolysis pattern is changed, larger molecules being formed at the lower temperatures, smaller ones at higher temperatures. At high temperatures small molecule formation is almost exclusive.

These conclusions are in agreement with those found by other workers.

### 3.3 The Effect of Residence Time on Pyrolysis

Sutton and Harris (20,21) investigated the effect of residence time on the extent of reaction and fragmentation pattern of the pyrolysis of a number of hydrocarbons, with the temperature kept constant. They found that, as the residence time was increased the extent of pyrolysis increased until 100% pyrolysis was approached. The changing pattern of pyrolysis was investigated by calculating the ratio of area of the methane peak to the total area of all other products of pyrolysis. They found that this ratio was residence (pyrolysis) time dependent and that it was larger at short





residence times that it is at long residence times. This means that at short residence times the production of methane is favored compared to the production of other pyrolysis products. At long residence time the production of other products is favored compared to methane production. Since methane is of minimal diagnostic value they concluded that most useful pyrograms could be obtained when long residence times were used.

Experiments were carried out to determine the most suitable residence time for the pyrolysis of the model compounds. The reactor temperature was kept constant, the reactor was quartz walled and was filled with iron coated Chromosorb W, 2,3-dimethylbutane was chosen as the model compound. The residence times chosen were 0.83 sec, 1.10 sec and 1.66 sec, this corresponded to flow rates of 30 ml/min, 20 ml/min., and 15 ml/min. The sample size injected was 0.4  $\mu$ l.

Table 3.4 shows the results of the experiment.

From Table 3.4, it is noticed that, as the residence time is increased the extent of pyrolysis increases. At a residence time of 0.83 seconds the extent of pyrolysis is 76%, when the residence time is doubled to 1.66 seconds the extent of pyrolysis increases to 85%.

Comparing the ratio of methane area to the total area of other pyrolysis products, this increases from 0.35 at a residence time of 0.83 seconds to 0.44 at a residence time of 1.66 seconds. This would indicate that methane formation



Table 3.4 The effect of residence time on the  
pyrolysis of 2,3-dimethylbutane at 690°C  
in an iron coated Chromosorb W packed reactor

Residence Time Products	1.66 sec.	1.10 sec.	0.83 sec.
Methane	0.26	0.21	0.19
Ethylene	0.08	0.08	0.04
Ethane	0.04	0.04	0.06
Propylene	0.35	0.34	0.33
2-Butene	0.08	0.07	0.07
2-Methyl-2-butene	0.05	0.06	0.06
2,3-Dimethylbutane	0.15	0.20	0.24
$\alpha$	0.85	0.80	0.76

is favored at higher residence times, and the production of other pyrolysis products favored at shorter residence times. This is in disagreement with the findings of Sutton and Harris.

Comparing the ratio of methane formed to 2-methyl-2-butene formed this changes from 3:1 at 0.83 seconds residence time to 5:1 at 1.66 seconds residence time. This would indicate that methane production is favored at longer residence times.

Since it was found that increase in the residence time leads to an increase in the minimally useful methane production it was decided to keep the residence time as small as possible. If the residence time was made too small then the



extent of pyrolysis would be adversely affected.

### 3.4 The Effect of Sample Size on Pyrolysis

The amount of sample injected into a pyrolysis reactor may have an effect in the pyrolysis results obtained. If the sample size is small then the peaks produced by the pyrolysis products on the recorder may be too small to measure. Gray (10) states that by decreasing the sample size, the possibility of methane formation is increased. He also states that

...the optimum sample size is such that there is no more than one sample molecule per thousand molecules of carrier gas... this is slightly less than one micro-litre of sample with normal carrier gas flow rates.

However if a large sample size is used, the possibility of incomplete pyrolysis and recombination products is increased. Kuelmans (14) has investigated the effect of sample size on the extent of secondary reaction product formation. He concludes that there is an optimum sample size at which the formation of secondary reaction products is minimal, and at which the peaks produced by the pyrolysis products are large enough to be measured.

A set of experiments were carried out to determine an optimum sample size for the reactor at the flow rates and reactor temperature to be used. Different amounts of 2,3-dimethylbutane were injected into the reactor to determine this optimum sample size. The reactor temperature was 690°C, the reactor was quartz walled and packed with iron coated Chromsorb W, the residence time was 1.66 seconds.





The results of the experiment to find the optimum sample size are tabulated in Table 3.5.

Table 3.5 The effect of sample size on pyrolysis of 2,3-dimethylbutane at 690°C in an iron coated Chromosorb W packed reactor

Sample Size Products	0.2 $\mu$ l	0.4 $\mu$ l	0.6 $\mu$ l	0.8 $\mu$ l
Methane	0.20	0.23	0.26	0.30
Ethylene	0.10	0.08	0.07	0.06
Ethane	0.01	0.04	0.02	0.03
Propylene	0.40	0.35	0.36	0.34
2-Butene	0.08	0.07	0.09	0.09
2-Methyl-2-butene	0.03	0.05	0.05	0.05
2,3-Dimethylbutane	0.11	0.15	0.15	0.17
$\alpha$	0.89	0.85	0.85	0.83

The data in Table 3.5 shows that as the sample size is decreased the extent of pyrolysis is increased. Thus a sample size of 0.2  $\mu$ l gives a 89% pyrolysis whereas a sample size of 0.8  $\mu$ l gives a 83% pyrolysis.

Comparing the amount of methane produced by the different sample sizes it will be noticed that this reaches a minimum when the sample size is 0.4  $\mu$ l. Sample sizes of 0.2  $\mu$ l and 0.8  $\mu$ l give more methane than either 0.4  $\mu$ l or 0.6  $\mu$ l.

The ratio of methane to 2-methyl-2-butene has a value





of 10:1 with a sample size of 0.2  $\mu$ l but drops to a value of 6:1 at a sample size of 0.8  $\mu$ l.

These results confirm that as the sample size is increased the extent of pyrolysis decreases. As the sample size is increased the amount of methane produced compared to the total amount of other pyrolysis products decreases. Thus small sample size increases the relative amount of methane formation. The absolute amount of methane formed reaches a minimum with a sample size of 0.4  $\mu$ l under the reaction conditions used.

### 3.5 The Effect of Material of Construction of Reactor on Pyrolysis

In a previous section the requisites of a material to be used as a reactor construction material were discussed. Two of the materials which meet the requirements and were readily available were quartz and steel. Two dimensionally identical reactors were packed with identical packing, the residence time in each was identical and the temperature of the reactor for each experiment was also identical. 0.6  $\mu$ l of the three model compounds were injected at each of the temperatures selected. Table 3.6A gives the results of pyrolysis of hexane, Table 3.6B of 2,2-dimethylbutane and Table 3.6C of 2,3-dimethylbutane

The residence times were, at 600°C 0.90 sec. at 650°C 0.83 sec. at 690°C 0.78 sec. at 750°C 0.72 sec.

The data tabulated in Table 3.6A, 3.6B and 3.6C shows



Table 3.6A Pyrolysis of hexane using quartz and steel walled reactors  
Packing material graphite 60-80 mesh

Temperature Products	600°C		650°C		690°C		750°C	
	Steel	Quartz	Steel	Quartz	Steel	Quartz	Steel	Quartz
Methane	0.02	0.05	0.07	0.07	0.14	0.17	0.32	0.31
Ethylene	0.05	0.03	0.20	0.21	0.38	0.38	0.28	0.33
Ethane	0.01	0.04	0.03	0.13	0.05	0.10	0.28	0.24
Propylene	0.02	0.06	0.13	0.21	0.19	0.22	0.03	0.07
2-Butene	0.02	0.02	0.08	0.07	0.06	0.05	0.00	0.00
2-Methyl-2-butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Pentene	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
Hexane	0.83	0.77	0.47	0.26	0.18	0.09	0.06	0.05
$\alpha$	0.17	0.23	0.53	0.74	0.82	0.91	0.94	0.95



Table 3.6B Pyrolysis of 2,2-dimethylbutane using quartz and steel walled reactors  
Packing material graphite

Temperature Products	600°C		650°C		690°C		750°C	
	Steel	Quartz	Steel	Quartz	Steel	Quartz	Steel	Quartz
Methane	0.00	0.02	0.07	0.12	0.19	0.17	0.34	0.36
Ethylene	0.01	0.02	0.10	0.12	0.21	0.20	0.29	0.39
Ethane	0.01	0.00	0.00	0.04	0.04	0.08	0.00	0.04
Propylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Butene	0.02	0.05	0.20	0.28	0.31	0.36	0.24	0.14
2-Methyl-2-butene	0.02	0.04	0.07	0.07	0.05	0.06	0.04	0.00
2,2-dimethylbutane	0.93	0.87	0.55	0.36	0.15	0.10	0.05	0.06
$\alpha$	0.07	0.13	0.45	0.64	0.85	0.90	0.95	0.94



Table 3.6C Pyrolysis of 2,3-dimethylbutane using quartz and steel walled reactors  
Packing material graphite

Temperature Products	600°C		650°C		690°C		750°C	
	Steel	Quartz	Steel	Quartz	Steel	Quartz	Steel	Quartz
Methane	0.01	0.03	0.11	0.19	0.23	0.27	0.32	0.31
Ethylene	0.05	0.00	0.05	0.08	0.16	0.15	0.28	0.33
Ethane	0.00	0.00	0.00	0.00	0.00	0.04	0.03	0.07
Propylene	0.06	0.13	0.29	0.34	0.40	0.33	0.28	0.24
2-Butene	0.00	0.00	0.06	0.11	0.07	0.10	0.03	0.00
2-Methyl-2-butene	0.03	0.08	0.13	0.10	0.06	0.04	0.03	0.00
2,3-Dimethylbutane	0.83	0.74	0.35	0.15	0.05	0.02	0.06	0.05
α	0.17	0.26	0.65	0.85	0.95	0.98	0.94	0.95
2,3-Dimethyl-1-butene	0.00	0.00	0.00	0.00	0.02	0.05	0.00	0.00





that the extent of reaction in the quartz walled reactor is always greater than that in the steel walled reactor. This difference is especially noticeable at lower temperatures and is noticed with all the model compounds used. In the pyrolysis of hexane the extent of reaction in the quartz walled reactor at 650°C is 74%, whilst in the steel walled reactor it is 53%. Thus there is a difference of 21% in the extent of reaction between the two reactors. The extent of pyrolysis of 2,2-dimethylbutane in the quartz walled reactor is 64% and in the steel walled reactor 45%; a difference of 19%. The extent of pyrolysis of 2,3-dimethylbutane in the quartz walled reactor at 650°C is 85% and in the steel reactor 65%; a difference of 20%. It is then noticeable that the extent of reaction in the quartz walled reactor is significantly higher than that in the steel walled reactor.

At higher temperatures this difference becomes less noticeable until at 750°C the extent of pyrolysis in the two reactors is the same. At this high temperature any effects on the extent of pyrolysis exerted by the material of construction are insignificant when compared to the temperature effect on the extent of pyrolysis.

The next consideration is to discuss the effect of the material of construction on the pyrolysis pattern.

In the pyrolysis of hexane the quartz walled reactor gives more 2 carbon atom molecules than the steel walled reactor. Taking the combined total of ethylene and ethane this is at 600°C is 6% in the steel walled reactor and 7% in



the quartz walled reactor. At 650°C these values are 23% and 34% respectively. The steel walled reactor gives slightly more 2-butene than the quartz walled reactor; 8% to 7% at 650°C, 6% to 5% at 690°C. The quartz walled reactor gives some 1-pentene which is the tell tale olefin (1) for hexane. The steel walled reactor gave no 1-pentene.

In the pyrolysis of 2,3-dimethylbutane the quartz walled reactor gave a greater amount of small molecule compounds compared to the steel walled reactor. The ratio methane/2-methyl-2-butene at 650°C is 0.9:1 in the steel reactor, and 2:1 in the quartz reactor. At 690°C this ratio is 3.8:1 in the steel reactor and 6.7:1 in the quartz walled reactor. The quartz walled reactor also gives more tell tale olefin than the steel walled reactor, in the case of 2,3-dimethylbutane the tell tale olefin is 2,3-dimethyl-1-butene

In the pyrolysis of 2,2-dimethylbutane the quartz walled reactor gives more small carbon atom molecules than the steel walled reactor. The ratio of methane/2 methyl-2-butene-2 at 650°C is 1:1 in the steel walled reactor and 2:1 in the quartz walled reactor. At 690°C this ratio is 4:1 in steel walled reactor and 3:1 in the quartz walled reactor. Thus at higher temperatures the steel walled reactor favors the production of smaller molecules, whereas this trend is not seen in the quartz walled reactor results.

The difference in the pyrolysis pattern of compounds in the two reactors are too small to say that in all cases the quartz walled reactor is better than the steel walled



reactor. Although the residence times and reactor temperatures were rigourously monitored and controlled to ensure reproducibility a small difference in either could cause the small differences seen in both the extent of pyrolysis and the pyrolysis pattern of the two reactors.



## CHAPTER IV

### RESULTS AND DISCUSSION: THE EFFECT OF REACTOR PACKING ON PYROLYSIS

In a previous section it was observed that no systematic investigation into the effect of reactor packing on the extent of pyrolysis and the pyrolysis pattern has been published. Various workers have used different reactor packings in their reactors. In this study three model compounds were pyrolyzed, under identical conditions of residence time and temperature, using different reactor packings. The reasons underlying the choice of reactor packings and model compounds were given in a previous section.

From the data presented in the previous section optimal conditions were chosen for the pyrolysis of hexane, 2,2-dimethylbutane, and 2,3-dimethylbutane. The temperatures chosen were 600°C, 650°C, 690°C and 750°C. The residence times chosen were 0.90 secs. at 600°C, 0.83 sec at 650°C, 0.78 sec at 690°C and 0.72 sec at 750°C. This corresponds to a flow rate of 30 ml /min . at the outlet of the analytical gas chromatograph. The sample size chosen was 0.6 microlitres.

The results of the experiments in which the model compounds were pyrolyzed using different reactor packings are given in Tables 4.1A and 4.1B, 4.2A, 4.2B, 4.3A and 4.3B. Tables 4.1A and 4.1B give the results of the pyrolysis of hexane, 4.2A and 4.2B the pyrolysis of 2,2-dimethylbutane and Tables 4.3A and 4.3B the pyrolysis of 2,3-dimethylbutane







The results given in tables sublettered A give the results of the pyrolysis using Chromsorb W 60-80 mesh, quartz wool and graphite 60-80 mesh packed reactors. Tables sublettered B give the results of pyrolysis using iron, iron coated Chromsorb W 60-80 mesh, and Chromsorb W 60-80 mesh packed reactors. Tables sublettered C give a summary of the data presented in tables sublettered A and B. The amount of each of the pyrolysis products formed as the temperature is increased is shown.

In the discussion of the data given in Tables 4.1A to 4.3B the following outline will be used. The effect of the reactor packing on the pyrolysis of hexane will be discussed first, followed by the discussion of the pyrolysis of 2,2-dimethylbutane then 2,3-dimethylbutane.

The discussion of the effect of the reactor packing on the pyrolysis of a model compound will be divided into two sub-sections. In the first, the effect of the reactor packing on the extent of pyrolysis at each reactor temperature will be discussed. The second sub-section will discuss the effect of the reactor packing on the pattern of pyrolysis. This will be done by discussing the variations in the amount of small molecule pyrolysis products and large molecule pyrolysis products formed with variations in temperature. The ratio of the amount of small molecule product to the amount of a large molecule product will be given. This gives an indication of the pyrolysis pattern in that it shows if the production of larger molecules or smaller molecules is favored.



## 4.1 The Effect of Reactor Packing on the Pyrolysis of Hexane

### 4.1.1 The Effect on the Extent of Pyrolysis

From the data tabulated in Tables 4.1A and 4.1B the extent of pyrolysis increases with temperature for all reactor packings.

At 600°C the extent of pyrolysis changes with reactor packing. Arranging the packings in increasing order of extent of pyrolysis gives the order Iron < Iron on Chromsorb W < Chromsorb W = Quartz Wool < Graphite. Thus Graphite packed reactor gives the greatest extent of reaction. The extent of reaction for the Chromsorb W and Quartz Wool reactors are identical, and the extent of reaction in the iron, and iron on Chromsorb W reactors are also the same.

At 650°C the reactor packings arranged in order of increasing extent of pyrolysis is Iron < Iron on Chromsorb W < Chromsorb W = Quartz Wool < Graphite. The Graphite packed reactor gives the greatest extent of pyrolysis, the iron packed reactor the least. The extent of reaction in the Chromsorb W reactor and Quartz Wool reactor are the same.

At 690°C the reactor packings arranged in order of increasing extent of pyrolysis is Iron < Iron on Chromsorb W < Quartz Wool < Chromsorb W < Graphite.

At 750°C the extent of reactions in all reactors is almost the same. The least extent of pyrolysis in the Iron on Chromsorb W reactor is 95% and the greatest extent of reaction is the graphite packed reactor 98%. At this high tempe-



Table 4.1A The effect of reactor packing on the pyrolysis of hexane  
A Chromsorb W packed reactor  
B Quartz wool packed reactor  
C Graphite packed reactor

Temperature Products	600°C			650°C			690°C			750°C		
	A	B	C	A	B	C	A	B	C	A	B	C
Methane	0.01	0.01	0.05	0.05	0.05	0.07	0.11	0.10	0.17	0.18	0.10	0.28
Ethylene	0.03	0.02	0.03	0.13	0.11	0.21	0.30	0.28	0.38	0.38	0.58	0.47
Ethane	0.00	0.01	0.04	0.03	0.03	0.13	0.05	0.05	0.10	0.07	0.03	0.06
Propylene	0.02	0.02	0.06	0.09	0.09	0.21	0.18	0.15	0.22	0.19	0.15	0.18
2-Butene	0.02	0.01	0.02	0.06	0.06	0.07	0.08	0.07	0.05	0.13	0.05	0.00
Hexane	0.92	0.92	0.77	0.64	0.64	0.26	0.28	0.35	0.09	0.05	0.04	0.02
α	0.08	0.08	0.23	0.36	0.36	0.74	0.72	0.65	0.91	0.95	0.96	0.98



Table 4.1B The effect of reactor packing on pyrolysis of hexane

A Iron packed reactor  
 B Iron coated Chromsorb W  
 C Chromsorb W

Temperature Products	600°C			650°C			690°C			750°C		
	A	B	C	A	B	C	A	B	C	A	B	C
Methane	0.01	0.01	0.01	0.02	0.03	0.05	0.09	0.16	0.11	0.24	0.35	0.18
Ethylene	0.01	0.01	0.03	0.04	0.08	0.13	0.13	0.20	0.30	0.47	0.34	0.38
Ethane	0.00	0.00	0.00	0.00	0.03	0.03	0.06	0.05	0.05	0.07	0.09	0.07
Propylene	0.02	0.02	0.02	0.05	0.06	0.09	0.11	0.12	0.18	0.14	0.13	0.19
2-Butene	0.00	0.00	0.02	0.03	0.03	0.06	0.00	0.07	0.08	0.04	0.03	0.13
Hexane	0.96	0.96	0.92	0.83	0.77	0.64	0.60	0.40	0.28	0.04	0.05	0.05
$\alpha$	0.04	0.04	0.08	0.17	0.23	0.36	0.40	0.60	0.72	0.96	0.95	0.95







Table 4.1C The effect of reactor packing on the pyrolysis of hexane

Reactor Packing Products	Iron	Iron on Chromsorb W	Chromsorb W	Quartz Wool	Graphite
Methane	Steady increase in amount formed with increase in temperature 600°C to 690°C. Sharp increase 690°C to 750°C.		Steady increase in amount formed with increase in temperature.		
Ethylene	Steady increase in amount formed with increase in temperature 600°C to 690°C. Sharp increase 690°C to 750°C.		Steady increase with increase in temperature		
Ethane	Steady increase from 600°C to 750°C	Steady increase 600°C to 690°C. Sharp increase 690°C to 750°C.	Steady increase in amount formed with increase in temperature.		
Propylene	Steady increase in amount formed with increase in temperature.		Steady increase 600°C to 690°C. Maximum formation at 690°C.	Reaches maximum at 690°C. Decrease as temperature increased.	
2-Butene	Steady increase in amount formed with increase in temperature.		Formation reaches maximum at 690°C. Decrease after this temperature with increase in temperature.		



rature the dominant factor in the pyrolysis is the temperature which renders insignificant any contribution to the breakdown of the hydrocarbon due to the reactor packing.

At all temperatures the greatest extent of pyrolysis of hexane was achieved using a graphite packed reactor. The least extent of reaction was achieved using an iron packed reactor. At lower temperatures the extents of pyrolysis in the Chromsorb W packed reactor and the Quartz Wool packed reactor are the same.

#### 4.1.2 The Effect on the Pyrolysis Pattern

The effect of the reactor packing on the pyrolysis pattern of hexane may be concluded from data tabulated in Tables 4.1A and 4.1B. In Table 4.1C the results are summarized, the effect of each reactor packing on the formation of a particular reaction product is shown.

In the pyrolysis of hexane, methane, ethylene and ethane are considered as small pyrolysis product molecules and propylene and 2-butene are considered large pyrolysis product molecules. The reactor packings and the effect each has on the product formation will be discussed in the order Iron, iron on Chromsorb W, Chromsorb W, quartz wool and graphite.

#### 4.1.3 Iron Packed Reactor

In the iron packed reactor the amounts of methane, ethylene and ethane formed rise slowly with increase in temperature from 600 to 690°C. Between 690°C and 750°C the amount



of methane produced rises sharply from 9% to 24%. The amount of ethylene formed increases sharply from 13% at 690°C to 47% at 750°C. The amount of ethane formed rises from 6% at 690°C to 7% at 750°C.

The amount of propylene produced by pyrolysis of hexane increases from 2% at 690°C to 14% at 750°C. This increase is gradual over the temperature range used. The amount of 2-butene increases with temperature from 0% at 600°C to 4% at 750°C.

The ratio methane formed: propylene product gives an indication of the amount of small molecule pyrolysis product formed to large molecule pyrolysis formed. This ratio is 0.5:1 at 600°C, 0.4:1 at 650°C, 1:1 at 690°C and 17:1 at 750°C. Thus at lower temperatures the production of propylene is favored over the production of methane.

#### 4.1.4 Iron Coated Chromsorb W

The amount of methane formed by pyrolysis of hexane in an iron coated Chromsorb W packed reactor increases with temperature. There is a large increase between 690°C and 750°C, the amount formed at 690°C is 16% and at 750°C 35%. Ethylene formation too shows a large increase between 690°C and 750°C from 20% at 690°C to 34% at 750°C. The amount of ethane formed rises from 5% at 690°C to 9% at 750°C.

The amount of propylene formed increases from 2% at 600°C to 13% at 750°C. The amount of 2-butene formed increases from 0% at 600°C to 3% at 750°C.





The methane: propylene ratio in the iron coated Chromsorb W reactor is 0.5:1 at 600°C, 3:1 at 650°C, 1.3:1 at 690°C and 2.6:1 at 750°C. Lower temperatures favor propylene production, higher temperatures favor methane production. The results of the pyrolysis of hexane in the iron packed reactor and the iron coated Chromsorb W reactor are similar both in extent and pattern of pyrolysis at all temperatures.

#### 4.1.5 Chromsorb W

In the Chromsorb W packed reactor the amount of methane formed by pyrolysis of hexane increases from 1% at 600°C to 18% at 750°C. The amount of ethylene formed increases steadily from 3% at 600°C to 38% at 750°C. The amount of ethane formed by pyrolysis increases from 0% at 600°C to 7% at 750°C.

The amount of propylene produced by pyrolysis of hexane increases from 2% at 600°C to 19% at 750°C. There is only a small increase in the amount of propylene formed by increasing the temperature from 690°C to 750°C. The amount of 2-butene formed increases from 2% at 600°C to 13% at 750°C.

The methane: propylene ratio is 0.5:1 at 600°C and 650°C, 0.6:1 at 690°C and 1:1 at 750°C. Thus at 600°C, 650°C and 690°C the production of propylene is favored compared to the production of methane in the pyrolysis of hexane.

#### 4.1.6 Quartz Wool

The results of the pyrolysis of hexane in a quartz wool packed reactor show the same pattern of pyrolysis regarding





the formation of methane, ethylene, ethane as in the Chromsorb W packed reactor.

The methane: propylene ratio is 0.5:1 at 600°C and 650°C, 0.6:1 at 690°C and 0.6:1 at 750°C. The results agree with that for the Chromsorb W packed reactor at all temperatures except 750°C. This is because in the quartz wool packed reactor the amount of methane and propylene formed remains steady in spite of an increase in temperature between 690°C and 750°C.

#### 4.1.7 Graphite Packed Reactor

The amount of methane formed by pyrolysis of hexane in a graphite packed reactor increases steadily from 5% at 600°C to 28% at 750°C. The amount of ethylene formed increases 3% at 600°C to 47% at 750°C. The amount of ethane formed rises from 4% at 600°C to 6% at 750°C.

The amount of propylene formed increases with temperature from 6% at 600°C to 22% at 690°C then decreases to 18% at 750°C. The amount of 2-butene formed increases from 2% at 600°C to a maximum of 7% at 650°C. The amount forms then decreases with increase in temperature, 5% is formed at 690°C and 0% at 750°C.

The methane: propylene ratio is 1:1 at 600°C, 0.3:1 at 650°C, 0.8:1 at 690°C and 1.5:1 at 750°C. For all temperatures except 750°C the production of propylene is favored compared to the production of methane.

Summarizing the effect of reactor packing on pyrolysis



the amount of methane, ethylene and ethane formed by the pyrolysis of hexane increases with increase in temperature. At higher temperatures only small amounts of large molecule size pyrolysis products are formed in the graphite packed reactor. In the iron packed reactor the amount of usefully diagnostic large molecule formed increases with temperature. This same pattern is seen in the iron coated Chromsorb W packed reactor. The Chromsorb W packed reactor and the quartz wool packed reactor show a different pattern in that the increase in larger molecules formed is only slight with increase in temperature above 690°C.

## 4.2 The Effect on Reactor Packing on the Pyrolysis of 2,2-dimethylbutane

### 4.2.1 The Effect on the Extent of Pyrolysis

From the data tabulated in Tables 4.2A and 4.2B the effect of reactor packing on the pyrolysis of 2,2-dimethylbutane may be determined. Table 4.2A gives pyrolysis data in reactors packed with Chromsorb W 60-80 mesh, quartz wool and graphite. Table 4.2B gives pyrolysis data in reactors packed with iron, iron on Chromsorb W and Chromsorb W.

Arranging the packings in increasing extent of reaction gives the following sequence: at 600°C Iron = Iron on Chromsorb W < Chromsorb W = Quartz Wool < Graphite; at 650°C Iron < Iron on Chromsorb W < Chromsorb W < Quartz Wool < Graphite; at 690°C Iron < Iron on Chromsorb W < Quartz Wool < Chromsorb W < Graphite. At 750°C all the reactor packings give approxi-



Table 4.2A The effect of reactor packing on the pyrolysis of 2,2-dimethylbutane  
A Chromsorb W packed reactor  
B Quartz wool packed reactor  
C Graphite Packed Reactor

<div> <div>Temperature</div> <div>Products</div> </div>	600°C			650°C			690°C			750°C		
	A	B	C	A	B	C	A	B	C	A	B	C
Methane	0.00	0.00	0.02	0.04	0.05	0.12	0.13	0.13	0.17	0.36	0.32	0.36
Ethylene	0.00	0.00	0.02	0.04	0.05	0.12	0.14	0.12	0.20	0.25	0.24	0.39
Ethane	0.00	0.00	0.00	0.02	0.00	0.04	0.10	0.03	0.08	0.11	0.04	0.04
2-Butene	0.02	0.02	0.05	0.09	0.12	0.28	0.23	0.24	0.36	0.20	0.10	0.14
2-Methyl-2-butene	0.02	0.02	0.04	0.07	0.07	0.07	0.09	0.10	0.06	0.05	0.13	0.14
2,2-Dimethylbutane	0.96	0.96	0.87	0.74	0.70	0.36	0.30	0.36	0.13	0.05	0.12	0.06
α	0.04	0.04	0.13	0.26	0.30	0.64	0.70	0.64	0.87	0.95	0.94	0.94



Table 4.2B    The effect of reactor packing on the pyrolysis of 2,2-dimethylbutane

A    Iron packed reactor  
 B    Iron coated Chromsorb W packed reactor  
 C    Chromsorb W packed reactor

<div> <div>Temperature</div> <div>Products</div> </div>	600°C			650°C			690°C			750°C		
	A	B	C	A	B	C	A	B	C	A	B	C
Methane	0.00	0.00	0.00	0.03	0.03	0.04	0.09	0.14	0.13	0.36	0.34	0.36
Ethylene	0.00	0.01	0.00	0.03	0.04	0.04	0.07	0.12	0.14	0.29	0.30	0.25
Ethane	0.00	0.00	0.00	0.00	0.01	0.02	0.04	0.05	0.10	0.09	0.09	0.11
2-Butene	0.01	0.01	0.02	0.05	0.08	0.09	0.15	0.21	0.23	0.18	0.20	0.20
2-Methyl-2-butene	0.01	0.00	0.02	0.03	0.03	0.07	0.00	0.05	0.09	0.00	0.00	0.05
2,2-Dimethylbutane	0.98	0.98	0.96	0.86	0.79	0.74	0.64	0.40	0.30	0.04	0.04	0.05
α	0.02	0.02	0.04	0.14	0.21	0.26	0.36	0.60	0.70	0.96	0.96	0.95







Table 4.2C The effect of reactor packing on the pyrolysis of 2,2-dimethylbutane

Reactor Packing Products	Iron	Iron on Chromsorb W	Chromsorb W	Quartz Wool	Graphite
Methane	Steady increase in amount formed with increase in temperature from 600°C to 690°C. Large increase from 690°C to 750°C.				Steady increase with increase in temperature.
Ethylene	Steady increase in amount formed with increase in temperature from 600°C to 690°C. Large increase from 690°C to 750°C.				Steady increase with increase in temperature.
Ethane	Steady increase in amount formed with increase in temperature.				Maximum amount formed at 690°C.
2-Butene	Steady increase with increase in temperature.	Maximum amount formed at 690°C.	Steady increase with temperature increase.	Maximum amount formed at 690°C.	Maximum amount formed at 690°C.
2-Methyl-2-butene	Maximum amount formed at 650°C.	Maximum amount formed at 690°C.		Steady increase with increase in temperature.	



mately the same extent of pyrolysis.

At all temperatures the graphite packed reactor gave the greatest extent of pyrolysis of the packings. The iron packed reactor gave the least extent of pyrolysis, the iron coated Chromsorb W packed reactor gave extents of pyrolysis midway between that found for the iron and Chromsorb W packed reactors. At 600°C the Chromsorb W and quartz wool reactors have the same extent of pyrolysis, at 650°C the extent of pyrolysis in the quartz Wool packed reactor is greater than that in the Chromsorb W packed reactor. This is reversed at 690°C so that the Chromsorb W packed reactor gave the greatest extent of pyrolysis.

#### 4.2.2 The Effect on the Pyrolysis Pattern

To investigate the effect of reactor packing on the pattern of pyrolysis the pyrolysis products are divided into two groups, the small molecules such as methane, ethylene and ethane and larger molecules such as 2-butene and 2-methyl-2-butene.

#### 4.2.3 Iron Packed Reactor

With an iron packed reactor the amount of methane formed rises slowly from 0% at 600°C to 9% at 690°C from 690°C to 750°C there is a rapid increase from 9% to 36%. The same pattern is observed for ethylene production which increases from 0% at 600°C to 7% at 690°C, at 750°C ethylene forms 29% of the products of pyrolysis.



The production of ethane rises steadily with temperature increasing from 0% at 600°C to 9% at 750°C.

In the iron packed reactor the formation of 2-butene increases from 1% at 600°C to 18% at 750°C. This increase occurs steadily over the whole temperature range. The production of 2-methyl-2-butene increases from 1% at 600°C to 3% at 650°C, this decreases to 0% at 690°C and 750°C.

The ratio of amount of 2 methyl-2-butene formed to amount of methane formed varies from 1:1 at 600°C; 1:1 at 650°C and 1:9 at 690°C. Thus the formation of methane is favored at all temperatures.

The methane:2-butene production ratio changes from 0.6:1 at 650°C to 0.6:1 at 690°C, to 2:1 at 750°C. Thus at high temperatures the production of methane is favored compared to the production of 2-butene.

#### 4.2.4 Iron Coated Chromsorb W

In the iron coated Chromsorb W reactor the amount of methane produced rises from 0% at 600°C steadily to 14% at 690°C, there is a great increase in production by increasing the temperature from 690°C to 750°C from 14% at 690°C to 34% at 750°C.

The production of ethylene and ethane at the different temperatures follows the same pattern as seen in the iron packed reactor.

The production of larger molecules in the iron coated Chromsorb W reactor is similar to that in the Chromsorb W





packed reactor. The amount of 2-butene formed in the iron coated Chromsorb W packed reactor increases with temperature from 600°C to 690°C, then decreases slightly from 690°C to 750°C. At 600°C 1% is formed, at 650°C 8%, at 690°C 21%, at 750°C 20%.

The production of 2-methyl-2-butene in the iron coated Chromsorb W packed reactor increases from 0% at 600°C to 3% at 650°C to 5% at 690°C, it then decreases at 750°C to 0%. This pattern is the same as the production of 2-methyl-2-butene in the Chromsorb W packed reactor.

#### 4.2.5 Chromsorb W

In the Chromsorb W packed reactor the production of methane increases steadily from 0% at 600°C to 13% at 690°C, then as the temperature is increased to 750°C the amount of methane formed rises to 36%.

The production of ethylene follows the same pattern, a steady increase from 0% at 600°C to 14% at 690°C; then a large increase to 25% at 750°C.

The amount of ethane formed rises steadily from 0% at 600°C to 11% at 750°C.

The amount of 2-butene formed rises steadily from 1% at 600°C to 18% at 750°C in the Chromsorb W packed reactor.

The amount of 2-methyl-2-butene formed rises steadily from 1% at 600°C to 9% at 690°C. At 750°C the amount of 2-methyl-2-butene formed is 5%.

The methane: 2-methyl-2-butene ratio changes from 1:2





at 600°C to 0.6:1 at 690°C to 1.4:1 at 690°C to 7:1 at 750°C. The production of methane is favored at higher temperatures are the production of 2-methyl-2-butene in the Chromsorb W packed reactor. The reverse is true for lower temperatures.

#### 4.2.6 Quartz Wool

The quartz wool packed reactor follows the same pattern of pyrolysis product formation as the Chromsorb W packed reactor as far as the production of methane and ethylene are concerned. As the temperature is increased from 600 to 690°C the amount of methane and ethylene formed increases. From 690°C to 750°C there is a large increase in the amount of methane and ethylene produced. The amount of ethane formed rises steadily from 0% at 650°C to 7% at 750°C.

The production of 2-butene in the quartz wool packed reactor follows the same pattern as that in the Chromsorb W packed reactor, a steady increase from 2% at 600°C to 24% at 690°C, at 750°C the amount produced drops to 20%.

The production of 2-methyl-2-butene in the quartz wool packed reactor follows a different pattern from that in Chromsorb W packed reactor. There is a steady increase in the amount formed from 2% at 600°C to 13% at 750°C.

The methane: 2-methyl-2-butene ratio is 0.8:1 at 650°C, 1.3:1 at 690°C and 2.8:1 at 750°C. Thus at higher temperatures the production of methane is favored compared to the production of 2-methyl-2-butene. At lower temperatures the reverse is true.



#### 4.2.7 Graphite

In the graphite packed reactor the production of methane and ethylene increase steadily with temperature. The amount of methane formed at 600°C is 2%, 12% at 650°C, 17% at 690°C and 36% at 750°C. The figures for ethylene production are 2% at 600°C, 12% at 650°C, 20% at 690°C and 39% at 750°C.

The amount of ethane produced by pyrolysis in the graphite packed reactor increases from 0% at 600°C to 8% at 690°C. At 750°C the amount formed has decreased to 4%.

The amount of 2-butene formed increased from 5% at 600°C to 36% at 690°C, then decreases at 750°C to 14%.

The amount of 2-methyl-2-butene increases with temperature from 4% at 600°C to 14% at 750°C.

The methane: 2-methyl-2-butene ratio is 0.5:1 at 600°C, 1.4:1 at 650°C, 3:1 at 690°C and 3.2:1 at 750°C. Thus at higher temperatures the production of methane is favored compared to the production of 2-methyl-2-butene in the graphite packed reactor.

Thus the graphite packed reactor is unique in that as the temperature is increased the amount of large molecule compounds produced by the pyrolysis of 2,2-dimethylbutane is increased.

#### 4.2.8 Summary

The Chromsorb W and quartz Wool packed reactors have similar breakdown patterns at all temperatures.

At low temperatures the iron coated Chromsorb W packed



reactor behaves as if it were a Chromsorb W reactor in its pyrolysis pattern of 2,2-dimethylbutane but at higher temperatures its breakdown pattern more closely resembles that of a Chromsorb W packed reactor.

#### 4.3 The Effect of Reactor Packing on the Pyrolysis of 2,3-dimethylbutane

##### 4.3.1 The Effect on the Extent of Pyrolysis

From the data tabulated in Tables 4.3A and 4.3B the effect of reactor packing on the pyrolysis of 2,3 dimethyl butane may be determined. Table 4.3A gives pyrolysis data in reactors packed with Chromsorb W 60-80 mesh, quartz wool and graphite. Table 4.3B gives pyrolysis data in reactors packed in Iron, Iron on Chromsorb and Chromsorb W.

Arranging the reactor packings in increasing extent of reaction gives the following sequence: at 600°C Iron = Iron on Chromsorb W < Chromsorb W = Quartz Wool < Graphite; at 650°C Iron on Chromsorb W = Iron < Chromsorb W < Quartz Wool < Graphite; at 690°C Iron < Iron on Chromsorb W < Quartz Wool < Chromsorb W < Graphite. At 750°C the extent of pyrolysis of 2,3-dimethylbutane is approximately the same in all reactors.

At all temperatures, except 750°C, the graphite packed reactor gives the greatest extent of pyrolysis of the packings used. The iron packed reactor gave the least extent of pyrolysis. At all the temperatures the extent of pyrolysis of 2,3-dimethylbutane in the Chromsorb W packed reactor was





Table 4.3A The effect of reactor packing on the pyrolysis of 2,3-dimethylbutane

A Chromsorb W packed reactor  
 B Quartz Wool packed reactor  
 C Graphite packed reactor

Temperature Products	600°C			650°C			690°C			750°C		
	A	B	C	A	B	C	A	B	C	A	B	C
Methane	0.03	0.02	0.02	0.19	0.09	0.07	0.27	0.11	0.20	0.31	0.33	0.20
Ethylene	0.00	0.00	0.00	0.08	0.02	0.02	0.15	0.03	0.14	0.33	0.25	0.16
Ethane	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.05	0.16	0.24	0.07	0.19
Propylene	0.13	0.03	0.04	0.34	0.16	0.16	0.33	0.30	0.22	0.07	0.20	0.17
2-Butene	0.00	0.05	0.00	0.11	0.03	0.02	0.10	0.13	0.17	0.00	0.08	0.16
2-Methyl-2-butene	0.08	0.00	0.00	0.10	0.16	0.14	0.04	0.15	0.05	0.00	0.03	0.05
2,3-Dimethylbutane	0.74	0.90	0.90	0.17	0.53	0.57	0.07	0.16	0.15	0.05	0.04	0.05
α	0.26	0.10	0.10	0.83	0.47	0.43	0.93	0.84	0.85	0.95	0.96	0.95





Table 4.3B The effect of reactor packing on the pyrolysis of 2,3-dimethylbutane

A Iron packed reactor  
 B Iron coated Chromsorb W packed reactor  
 C Chromsorb W packed reactor

Temperature Products	600°C			650°C			690°C			750°C		
	A	B	C	A	B	C	A	B	C	A	B	C
Methane	0.00	0.00	0.02	0.08	0.06	0.07	0.13	0.19	0.20	0.50	0.47	0.20
Ethylene	0.00	0.00	0.00	0.04	0.02	0.02	0.05	0.04	0.14	0.17	0.18	0.16
Ethane	0.00	0.00	0.00	0.00	0.00	0.02	0.05	0.06	0.16	0.04	0.07	0.19
Propylene	0.02	0.02	0.04	0.14	0.15	0.16	0.30	0.33	0.22	0.22	0.21	0.17
2-Butene	0.00	0.00	0.00	0.02	0.02	0.02	0.03	0.07	0.17	0.03	0.04	0.16
2-Methyl-2-butene	0.02	0.02	0.04	0.07	0.07	0.14	0.06	0.06	0.05	0.00	0.00	0.05
2,3-Dimethylbutane	0.96	0.96	0.90	0.65	0.66	0.57	0.37	0.24	0.15	0.04	0.04	0.05
α	0.04	0.04	0.10	0.35	0.34	0.43	0.63	0.76	0.85	0.96	0.96	0.95



Table 4.3C The effect of reactor packing on the pyrolysis of 2,3-dimethylbutane

Reactor Packing Products	Iron	Iron on Chromsorb W	Chromsorb W	Quartz Wool	Graphite
Methane	Steady increase in amount formed with increase in temperature 600°C to 690°C. Large increase 690°C to 750°C.	Steady increase in amount formed with increase in temperature 600°C to 690°C. Large increase 690°C to 750°C.	Steady increase to 690°C. No further increase.	Steady increase 600°C to 690°C. Large increase 690°C to 750°C.	Steady increase with increase in temperature.
Ethylene	Steady increase in amount formed with temperature increase 600°C to 690°C. Large increase 690°C to 750°C.	Steady increase with increase in temperature.			
Ethane	Maximum amount produced at 690°C.		Steady increase in amount formed with increase in temperature		Steady increase 600°C to 690°C. Large increase 690°C to 750°C.
Propylene	Maximum amount formed at 690°C				
2-Butene	Maximum amount formed at 690°C				
2-Methyl-2-butene	Maximum formed at 690°C.	Maximum formed at 650°C.			80



similar to that in the quartz wool reactor, i.e., at 650°C Chromsorb W gave 43%, quartz wool 47%, at 690°C Chromsorb W 85%, quartz wool 84%.

#### 4.3.2 The Effect on the Pyrolysis Pattern

The effect of changing the reactor packing on the pyrolysis pattern of 2,3-dimethylbutane may be determined from the data tabulated in Tables 4.3A and 4.3B.

#### 4.3.3 Iron

In the iron packed reactor the amount of methane formed rises from 0% at 600°C to 50% at 750°C. The increase from 600°C to 690°C is gradual but there is a large increase in the amount of methane formed from 690°C to 750°C. At 690°C 13% of the total pyrolysis products and unpyrolyzed parent is methane, at 750°C this figure is increased to 50%.

The amount of ethylene formed in the pyrolysis increases from 0% at 600°C to 17% at 750°C in the iron packed reactor. The amount of ethylene produced rises steadily from 0% at 600°C to 5% at 690°C. There is a large increase in the amount of ethylene formed between 690°C and 750°C. The amount of ethane formed by pyrolysis increases from 0% at 650°C to 5% at 690°C, then drops to 4% at 750°C.

The amount of propylene formed in the iron packed reactor reaches a maximum at 690°C of 30% then falls to 22% at 750°C. The amount of 2-butene formed increases from 0% at 600°C to 3% at 690°C. The amount of 2-methyl-2-butene formed





increase in temperature. The amount of ethylene formed increases from 0% at 600°C to 16% at 750°C. The increase between the temperatures 650°C and 690°C is large. The amount of ethane formed by pyrolysis increases from 0% at 600°C to 19% at 750°C.

The amount of propylene formed by pyrolysis reaches a maximum of 22% at 690°C then drops to 17% at 750°C.

The amount of 2-butene formed increases with temperature to 17% at 690°C from 0% at 600°C. At 750°C 16% of the total pyrolysis products is 2-butene.

The amount of 2-methyl-2-butene formed increases from 4% at 600°C to 14% at 650°C. It then decreases with increase in temperature to 5% at 690°C.

The methane: 2-methyl-2-butene ratio is 0.5:1 at 600°C and 650°C, 4:1 at 690°C and 750°C. Thus at 600°C and 650°C the formation of 2-methyl-2-butene is favored compared to the formation of methane.

#### 4.3.6 Quartz Wool

The quartz wool packed reactor shows a slightly different pyrolysis pattern for the pyrolysis of 2,3-dimethylbutane than the Chromsorb W packed reactor.

The amount of methane produced by pyrolysis of 2,3-dimethylbutane increase sharply from 11% at 690°C to 33% at 750°C. The increases from 2% methane produced at 600°C to 11% at 690°C is steady.

The ethylene production increases steadily from 6% at





reaches a maximum of 7% at 650°C, then drops to 60% at 690°C and 0% at 750°C.

The methane: 2-methyl-2-butene ratio is 1:2 at 600°C, 1.1:1 at 650°C, 2.1:1 at 690°C and 50:1 at 750°C. Thus the iron packed reactor favors the production of larger molecules at low temperatures and the almost exclusive production of small molecules at high temperatures.

#### 4.3.4 Iron Coated Chromsorb W

The iron coated Chromsorb W packed reactor shows the same features as the iron packed reactor. The large increase in methane and ethylene formation between 690 and 750°C. The amount of ethane produced however increases with temperature, which is in contrast to the iron packed reactor in which ethane production reaches a maximum at 690°C.

The production of propylene, 2-butene and 2-methyl-2-butene in the iron coated Chromsorb W packed reactor shows the same pattern as in the iron packed reactor. The amount of species formed reaches a maximum then decreases with a further increase in temperature.

The methane: 2-methyl-2-butene ratio is 1:2 at 600°C, 1.9:1 at 650°C, 3:1 at 690°C and 47:1 at 750°C.

#### 4.3.5 Chromsorb W

The amount of methane formed by pyrolysis of 2,3-dimethylbutane in the Chromsorb W packed reactor increases from 2% at 600°C to 20% at 690°C. This value remains steady with



600°C to 25% at 750°C. The ethane production too is increased steadily from 0% at 600°C to 7% at 750°C.

The production of propylene follows the same pattern as in the Chromsorb W packed reactor. A steady increase to a maximum of 30% at 690°C, then a decrease to 20% at 750°C.

The amount of 2-butene formed reaches a maximum of 13% at 690°C then drops to 8% at 750°C. The amount of 2-methyl-2-butene formed reaches a maximum at 650°C.

The methane: 2 methyl-2-butene ratio in the quartz wool packed reactor is 2:1 at 600°C, 0.4:1 at 650°C, 0.8:1 at 690°C and 11:1 at 750°C. Thus 650°C is the optimum temperature for 2 methyl-2-butene production.

#### 4.3.7 Graphite

In the graphite packed reactor the amount of methane produced by pyrolysis increases steadily from 3% at 600°C to 31% at 750°C. The amount of ethylene too increases steadily from 0% at 600°C to 33% at 750°C. The amount of ethane produced increases steadily from 0% at 600°C to 4% at 690°C. Then there is a great increase with increase in temperature so that 24% is produced at 750°C.

Propylene production reaches a maximum of 33% at 690°C then falls to 7% at 750°C. This decrease in the amount of propylene formed between 690°C and 750°C is the largest of any of the reactors packings used.

The amount of 2-butene formed reaches a maximum at 650°C of 11% then falls to 0% at 750°C.



The amount of 2 methyl butene 2 formed reaches a maximum at 650°C of 10% then drops to 0% at 750°C.

The one noticeable feature about the pyrolysis of 2,3-dimethylbutane in a graphite packed reactor compared to the pyrolysis in other reactors is the complete absence of high temperatures of any larger molecules such as 2-butene.

The methane: 2-methyl-2-butene ratio is 0.4:1 at 600°C, 2:1 at 650°C, 7:1 at 690°C and 31:1 at 750°C.

Thus the production of 2 methyl-2-butene is optimized at 600°C in the graphite packed reactor.

#### 4.3.8 Summary

In all reactors the production of diagnostically useful olefins from the pyrolysis of 2,3-dimethylbutane reaches a maximum proportion at the lower temperatures used. In some reactors used the olefins produced are of minimal diagnostic value at high temperatures.

#### 4.4 Summary

From the previous sections it is concluded that changes in reaction conditions change the extent and pattern of pyrolysis of the compounds used.

An increase in the temperature of the reactor will cause an increase in the extent of pyrolysis if all the other variables such as residence time, amount injected and reactor packing remain constant. As the temperature is increased so the formation of smaller molecules such as methane is





avored over the production of larger molecules such as 2-butene in the pyrolysis of the compounds used.

As the residence time is increased, the other variables being kept constant, the extent of pyrolysis increases. There is at a particular temperature and sample size an optimum residence time in which the production of larger molecules is favored compared with the production of small molecules.

As the sample size is increased, the extent of pyrolysis decreases, if other variables are kept constant.

Of the reactor packings used graphite consistently gave the greatest extent of pyrolysis, this holds true for all temperatures except 750°C and all model compounds. The difference between the extent of pyrolysis in the graphite packed reactor and the iron packed reactor at the same temperature can be as much as 40% as in the case of the pyrolysis of 2,2-dimethylbutane at 650°C. The iron packed reactor gave the lowest extent of pyrolysis for all compounds.

The extent of pyrolysis in the Chromsorb W packed reactor and the quartz wool packed reactor are similar. In a few cases the difference in extent of pyrolysis of the same compound at the same temperature exceeds 8%. This is to be expected since both Chromsorb W and quartz wool have large surface areas.

The extent of pyrolysis on an iron coated Chromsorb W packed reactor is in all cases between the extent of pyrolysis in the Chromsorb W packed reactor and the iron packed reactor. It is always greater than the iron packed reactor





and less than the Chromsorb W reactor. This could be explained by postulating the existence of active catalytic sites on the surface of the Chromsorb W and the absence of such sites on the surface of the iron. The active catalytic sites increase the extent of pyrolysis. By coating the Chromsorb W with iron some of these active sites are removed and the extent of pyrolysis is lowered compared to that in the uncoated Chromsorb W packed reactor. However not all active sites are removed, so the extent of pyrolysis in the iron coated Chromsorb W reactor is always greater than that in the iron packed reactor.

The data for the graphite packed reactor may be explained by the possibility that it has the largest surface area of the packing materials used. Thus since there is more surface to react on, the pyrolysis of the compound is increased.

2,2-dimethylbutane gave the lowest extents of pyrolysis of the model compounds at 600, 650 and 690°C, and with all reactor packings.

At 750°C the extent of pyrolysis for a compound was independent of reactor packing. Thus any effect on pyrolysis that the packing has at lower temperatures is insignificant compared to the effect of the high temperature on pyrolysis.

When the extent of pyrolysis of the model compounds in an iron packed reactor between the temperatures of 690°C and 750°C is compared to the extent of pyrolysis on any other



packed reactor between 690°C and 750°C, the following observation holds for all model compounds and all packings. At 690°C the extent of pyrolysis in the iron packed reactor is much less than that using any other packed reactor. At 750°C the extent of pyrolysis the two reactors are nearly identical. This means that between 690°C and 750°C the iron exerts a catalytic effect on the pyrolysis of the compound causing a large increase in the extent of pyrolysis. The differences in the extents of reaction of the same model compound under identical reaction conditions with different reactor packings is partly related to the surface area of the packing. Iron which has a low surface area has a low extent of pyrolysis. Graphite which has a high extent of pyrolysis has a large surface area. To verify that the surface area is a controlling factor surface area measurements would have to be made.

However it is impossible to explain the difference in pyrolysis patterns on the grounds of surface area alone. One possibility may be the presence of catalytically active sites on the surface of the reactor packing catalyses the breakdown depending on the number and nature of the active site on the surface of the reactor packing. This difference in the pyrolysis pattern is seen in Figures 4.1, 4.2 and 4.3. The pattern in the iron, Chromsorb W and the graphite packed reactors is shown. The pattern in the iron coated Chromsorb W packed reactor and the iron packed reactor are similar, as is the pattern in the Chromsorb W and quartz wool packed reactors. Figure 4.1 shows the effect on the packing on the formation of ethylene



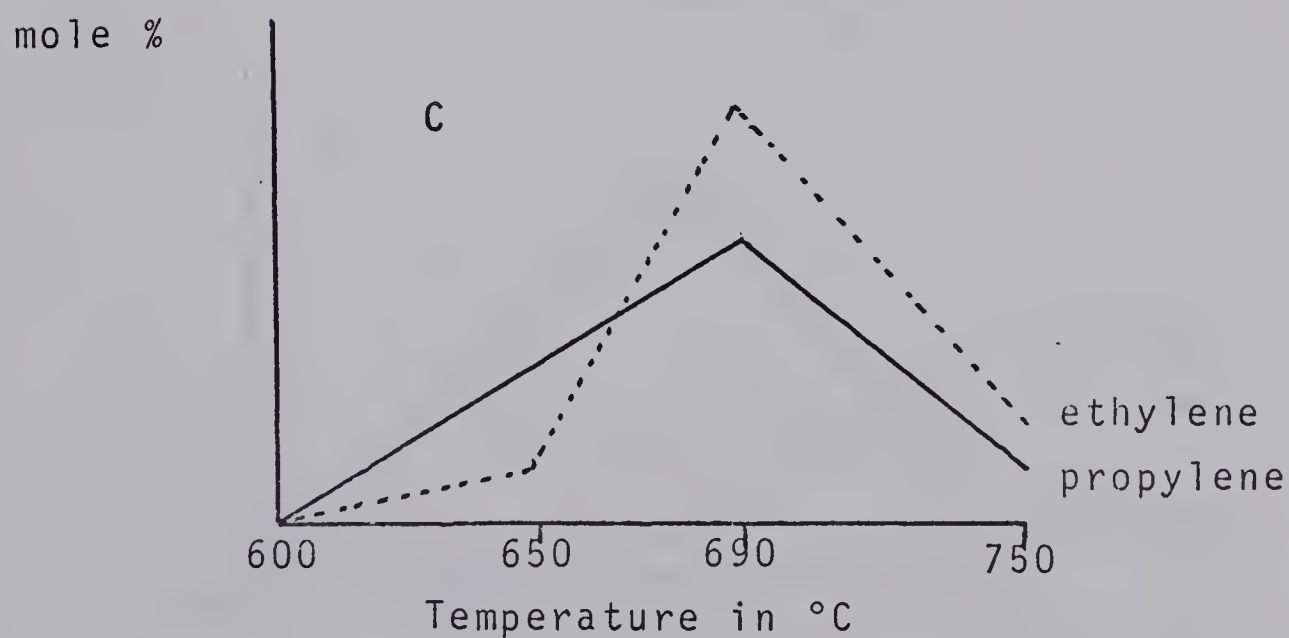
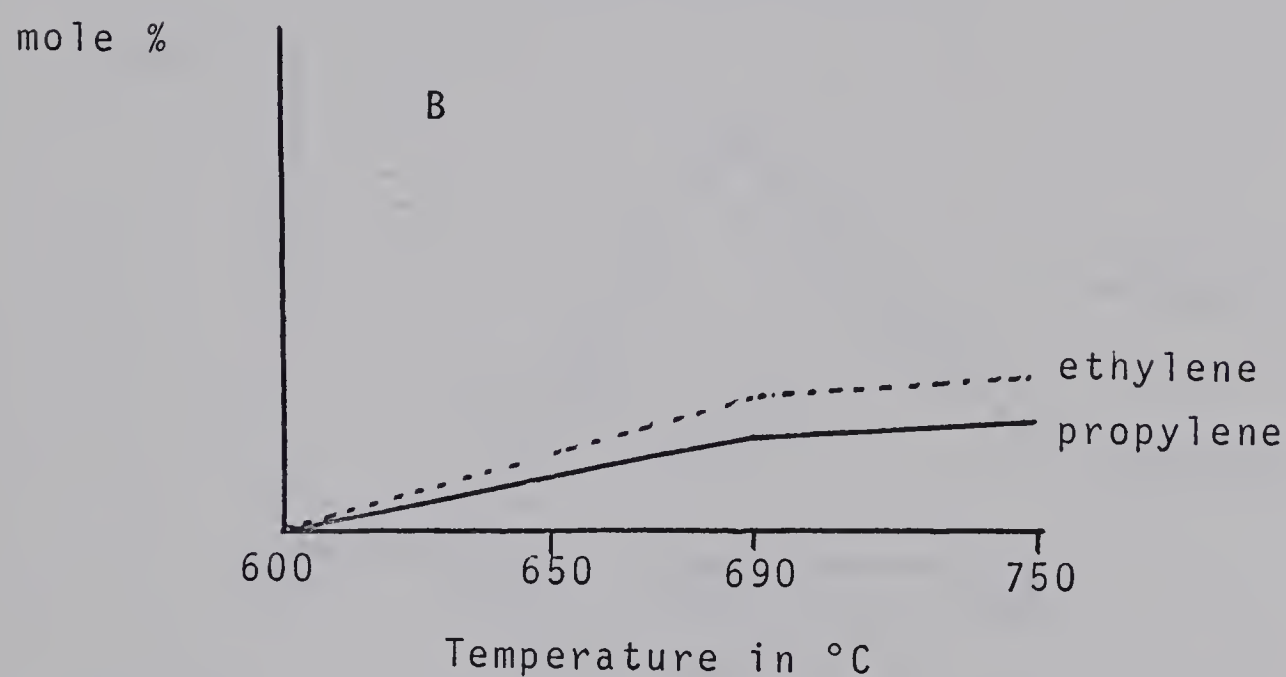
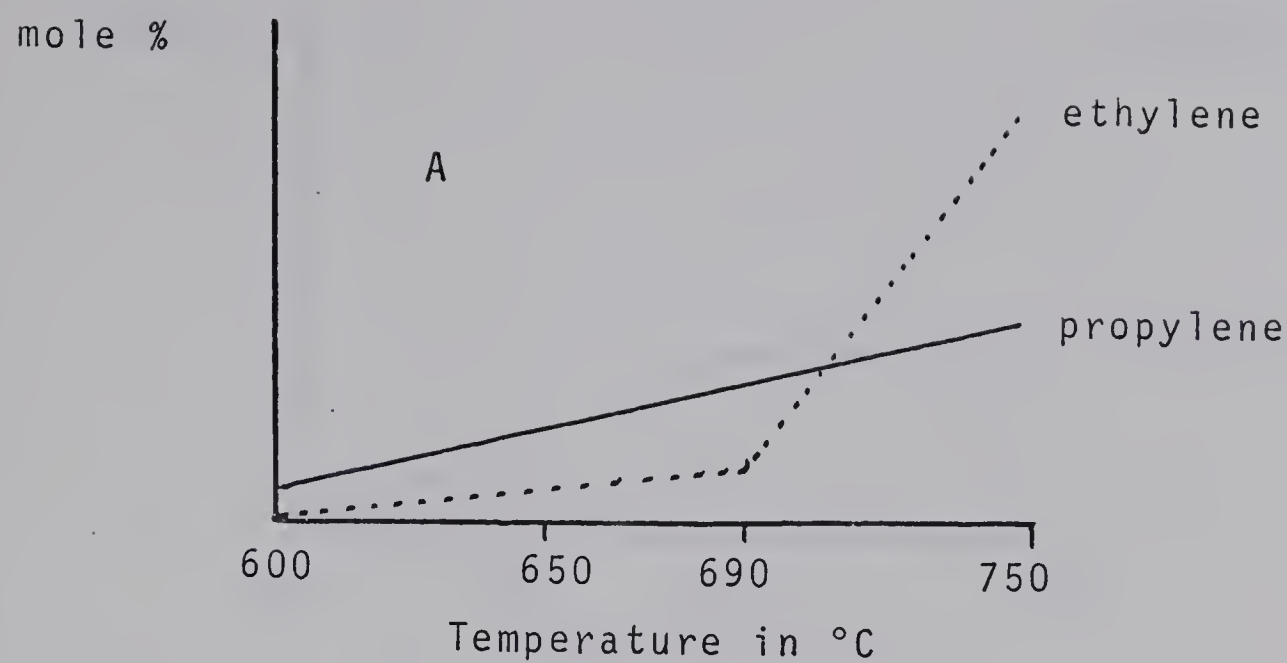
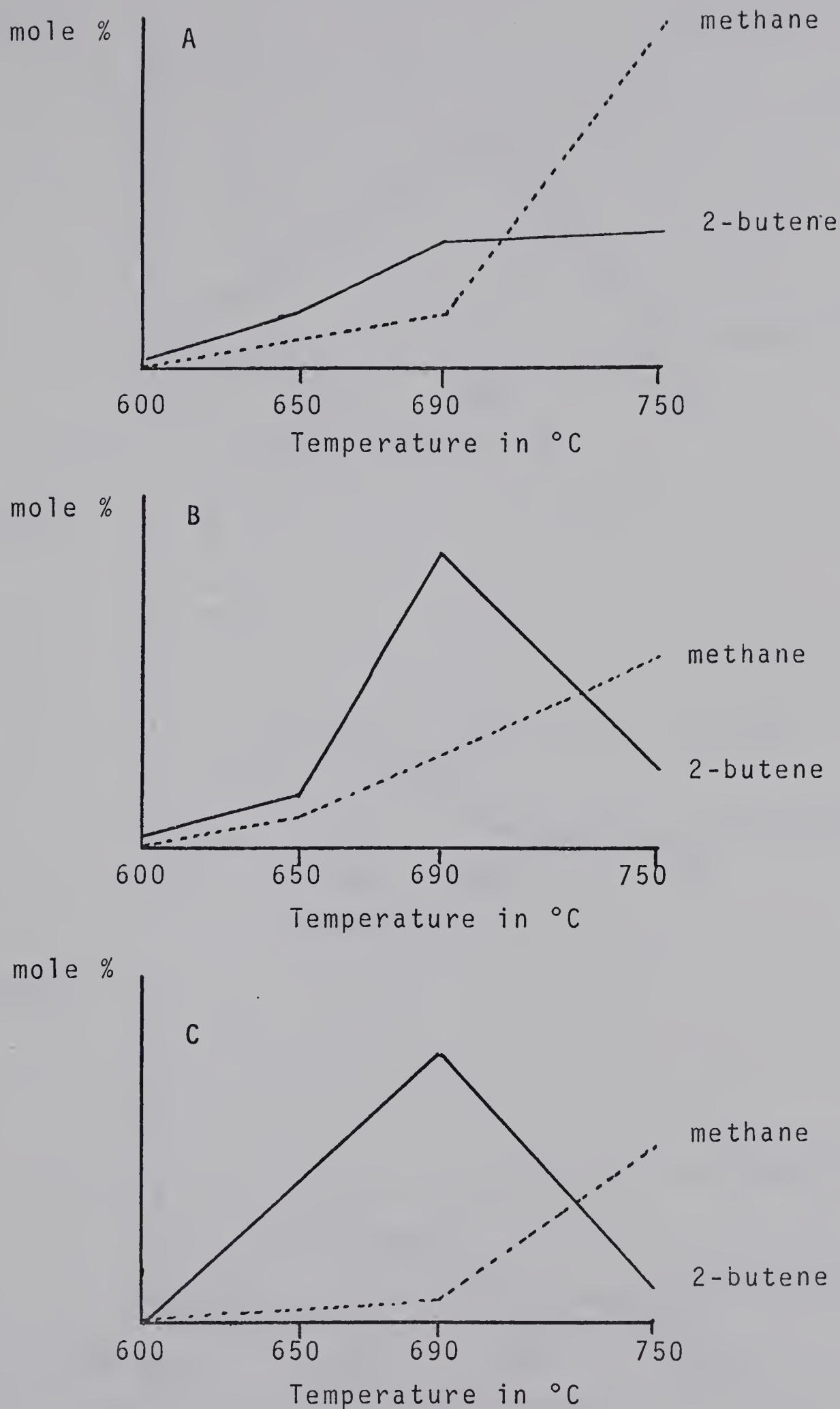


Figure 4.1 The effect of reactor packing on the formation of ethylene and propylene from the pyrolysis of hexane

- A Iron packed reactor
- B Chromsorb W packed reactor
- C Graphite packed reactor





**Figure 4.2** The effect of reactor packing on the formation of methane and 2-butene from the pyrolysis of 2,2-dimethylbutane

- A Iron packed reactor
- B Chromsorb W packed reactor
- C Graphite packed reactor





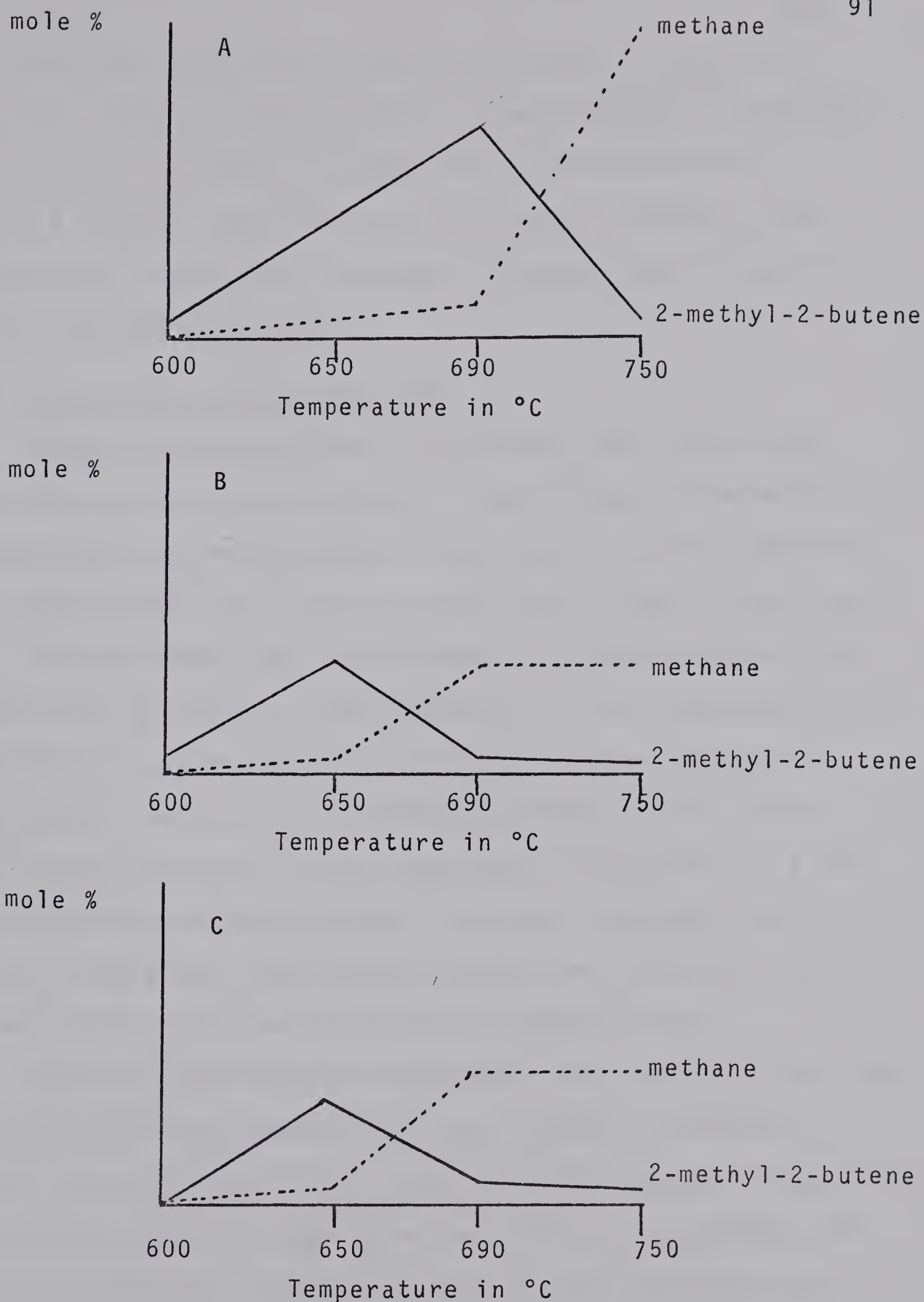


Figure 4.3 The effect of reactor packing on the formation of methane and 2-methyl-2-butene from the pyrolysis of 2,3-dimethylbutane

- A Iron packed reactor
- B Chromsor W packed reactor
- C Graphite packed reactor



and propylene from the pyrolysis of hexane. Figure 4.2 shows the effect of the packing on the formation of methane and 2-butene from the pyrolysis of 2,2-dimethylbutane. Figure 4.3 shows the effect of the reactor packing on the formation of methane and 2-methyl-2-butene from the pyrolysis of 2,3-dimethylbutane.

#### 4.5 Suggestions for Further Work

Several possible areas for further work can be seen from the results and discussion. The effect on the material of construction on the extent of pyrolysis and the pyrolysis was investigated for a quartz walled and a steel walled reactor. It was shown that the material of construction of the reactor has an effect on the pyrolysis of the compounds used. The effect of other materials of construction could be investigated, the obvious investigation would be the effect of gold on the pyrolysis of the compounds. As stated in a previous section the gold reactor is usually unpacked and so the effect of packing a gold walled reactor on the extent and pattern of pyrolysis would be worth investigating.

Another investigation that would be useful would be the effect of different amounts of iron coated on Chromsorb W. In the present investigation only one iron coated Chromsorb W reactor was used. It should be possible to investigate the effect on different amounts of iron on the Chromsorb W on the extent of pyrolysis and the pyrolysis pattern.

The effect of reactors packed with two or more reactor packings could be investigated. It may be possible that by



using a reactor packed with more than one packing to obtain a more useful pyrogram than was possible by the use of one reactor packing.



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## APPENDIX



Computer program for the calculation of  $\alpha$  , the degree of reaction and the % composition of the pyrolysis products.

```

      INTECAL :PROCEDURE  OPTIONS(MAIN);
DCL  (AREA(10),   CAREA(10),
R(10),MOLEF(10))DECIMAL FLOAT
      ,NAME(10)CHARACTER(50),HEADING(2)CHARACTER(80) ;
ON ENDFILE(SCARDS)GO TO B;
      GET FILE (SCARDS)EDIT(HEADING)(2 A(80));
PUT FILE (SPRINT)EDIT          (HEADING)(A(80),
SKIP,A(80)); A:
GET FILE  (SCARDS) EDIT(N,(NAME(J),AREA(J)
R(J) DO J=1 TO N))
(F(80),(N)(A(50),F(20,4),F(10,4)));
SUM=0;
DO J=1 TO N;
CAREA(J)=AREA(J)*R(J);
SUM=SUM+CAREA(J) ;
END;
DO J=1 TO N;
MOLEF(J)=CAREA(J)/SUM;
END;
PUT FILE (SPRINT)EDIT('COMPOUND','AREA
      CAREA      MOLE FRACTIONS')
(SKIP(3),A,X(46),A);
PUT FILE (SPRINT)EDIT((NAME(J),AREA(J),
CAREA(J), MOLEF(J)
DO J=1 TO N), SUM)
(SKIP,(N)(SKIP,A(50),
3 F(10,4)),SKIP,F(10,4));
GO TO A; B:
END INTECAL;

```







**B30013**